

# NUMERICAL CALCULATIONS OF MOLECULAR ORBITALS

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[Manuscript received February 22, 1954]

## Summary

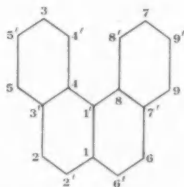
The molecular orbitals of 3,4-benzophenanthrene are determined in order to illustrate in detail the use of the alternant and symmetry properties of a molecule to simplify the numerical calculations.

## I. INTRODUCTION

The determination of the molecular orbitals of a molecule involves the calculation of the eigenvalues (m.o. binding energies) and eigenvectors (molecular orbital coefficients) of the secular matrix of the molecule. This eigenvalue problem has been solved for various molecules but since little more than the final numerical results have ever been published, the best method to use in carrying out the actual calculations may not be obvious to the theoretical chemist unfamiliar with matrix algebra. It is the purpose of the present paper to remedy this situation by discussing in detail the determination of the molecular orbitals of 3,4-benzophenanthrene. The eigenvalue problem for this molecule is a typical one and its solution using the method recently proposed by Potts (1953) will illustrate the advantages of this method, as well as the use of symmetry properties of the molecule to simplify the calculations.

## II. SECULAR MATRIX

Since 3,4-benzophenanthrene is an alternant hydrocarbon (Coulson and Rushbrooke 1940) its 18 carbon atoms can be numbered 1, 2, . . . , 9, 1', 2', . . . , 9' such that nearest neighbours of an undashed number are dashed numbers and vice versa, for example,



With the atomic orbitals ordered  $\varphi(1), \varphi(2), \dots, \varphi(9), \varphi(1'), \varphi(2'), \dots, \varphi(9')$  this assures that the secular matrix **A** is of the form

$$\mathbf{A} = \begin{bmatrix} \mathbf{O} & \mathbf{B} \\ \mathbf{B}' & \mathbf{O} \end{bmatrix}, \dots\dots\dots (1)$$

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where  $\mathbf{O}$  is the  $9 \times 9$  zero matrix,  $\mathbf{B}'$  the transpose of  $\mathbf{B}$ , and

$$\mathbf{B} = \begin{matrix} & \begin{matrix} \varphi(1') & \varphi(2') & \varphi(3') & \varphi(4') & \varphi(5') & \varphi(6') & \varphi(7') & \varphi(8') & \varphi(9') \end{matrix} \\ \begin{matrix} \varphi(1) \\ \varphi(2) \\ \varphi(3) \\ \varphi(4) \\ \varphi(5) \\ \varphi(6) \\ \varphi(7) \\ \varphi(8) \\ \varphi(9) \end{matrix} & \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \end{matrix} \quad \dots \quad (2)$$

It has been assumed, as is customary, that the elements of the matrix  $\mathbf{A}$  are the resonance integrals  $\int \varphi(i) H \varphi(j) d\tau$  equal to unity if  $i$  and  $j$  are nearest neighbours and otherwise zero ( $H$  is the effective Hamiltonian corresponding to the total energy of a  $\pi$ -electron).

As proved by Potts (1953) the eigenvalue problem can be formulated as follows: determine the eigenvalues  $\lambda^2$  and the eigenvectors  $\mathbf{u}$  normalized to length  $\sqrt{\frac{1}{2}}$  of  $\mathbf{B}\mathbf{B}'$ ; determine the vector  $\mathbf{v}$  from the relation  $\mathbf{B}'\mathbf{u} = \lambda\mathbf{v}$ ; then the eigenvalues of  $\mathbf{A}$  are  $\pm\lambda$  and the corresponding eigenvectors, normalized to length 1, are  $\begin{bmatrix} \mathbf{u} \\ \pm\mathbf{v} \end{bmatrix}$ . The eigenvalue problem is accordingly reduced from one in 18 dimensions to one in 9 dimensions.

### III. SYMMETRY

The symmetry of the molecule about a vertical axis enables the matrix  $\mathbf{B}\mathbf{B}'$  to be reduced to a direct sum with a consequent simplification of the eigenvalue problem (see, for example, Hückel 1932). The symmetry relates atoms numbered 2 and 6, 3 and 7, 4 and 8, 5 and 9, and similarly for the dashed numbers. Instead of the normalized orthogonal sequence of atomic orbitals  $\varphi(1), \dots, \varphi(9')$ , one introduces a new normalized orthogonal sequence:

$$\left. \begin{aligned} \chi(1) &= \varphi(1), \\ \chi(2) &= \frac{1}{\sqrt{2}}\{\varphi(2) + \varphi(6)\}, & \chi(6) &= \frac{1}{\sqrt{2}}\{\varphi(2) - \varphi(6)\}, \\ \chi(3) &= \frac{1}{\sqrt{2}}\{\varphi(3) + \varphi(7)\}, & \chi(7) &= \frac{1}{\sqrt{2}}\{\varphi(3) - \varphi(7)\}, \\ \chi(4) &= \frac{1}{\sqrt{2}}\{\varphi(4) + \varphi(8)\}, & \chi(8) &= \frac{1}{\sqrt{2}}\{\varphi(4) - \varphi(8)\}, \\ \chi(5) &= \frac{1}{\sqrt{2}}\{\varphi(5) + \varphi(9)\}, & \chi(9) &= \frac{1}{\sqrt{2}}\{\varphi(5) - \varphi(9)\}, \end{aligned} \right\} \quad \dots \quad (3)$$

as well as  $\chi(1'), \dots, \chi(9')$  similarly defined.  $\chi(2)$  and  $\chi(6)$ , for example, have the property that  $\chi(2)$  is invariant and  $\chi(6)$  merely changes sign when the numbers 2 and 6 are interchanged.

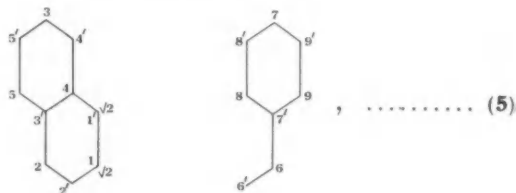
The transformed matrix is

$$\begin{array}{c}
 \chi(1) \\
 \chi(2) \\
 \chi(3) \\
 \chi(4) \\
 \chi(5) \\
 \chi(6) \\
 \chi(7) \\
 \chi(8) \\
 \chi(9)
 \end{array}
 \begin{array}{c}
 \chi(1') \quad \chi(2') \quad \chi(3') \quad \chi(4') \quad \chi(5') \quad \chi(6') \quad \chi(7') \quad \chi(8') \quad \chi(9') \\
 \left[ \begin{array}{ccccccccc}
 1 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\
 \sqrt{2} & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
 \hline
 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1
 \end{array} \right] \dots (4)
 \end{array}$$

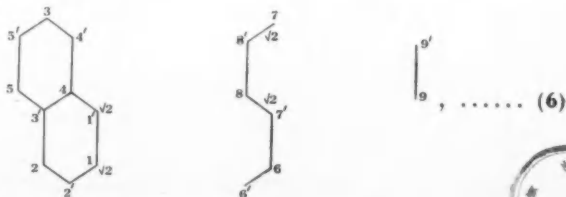
whose elements are the resonance integrals

$$\begin{aligned}
 \int \chi(1) H \chi(1') d\tau &= \int \varphi(1) H \varphi(1') d\tau = 1, \\
 \int \chi(1) H \chi(2') d\tau &= \frac{1}{\sqrt{2}} \int \{ \varphi(1) H \varphi(2') + \varphi(1) H \varphi(6') \} d\tau = \sqrt{2}, \\
 \int \chi(1) H \chi(6') d\tau &= \frac{1}{\sqrt{2}} \int \{ \varphi(1) H \varphi(2') - \varphi(1) H \varphi(6') \} d\tau = 0, \text{ etc.}
 \end{aligned}$$

The matrix appears as a direct sum of a  $5 \times 5$  and a  $4 \times 4$  matrix. The significance of this decomposition is made evident if one writes down the "molecule" corresponding to this matrix, namely,



where the label  $\sqrt{2}$  on a bond indicates a resonance integral of  $\sqrt{2}$  instead of unity. The use of the symmetry property has enabled the molecule to be "split" into two separate parts, the "broken" bonds being compensated by the factor  $\sqrt{2}$ . The right-hand portion is still symmetric so that another division is possible giving finally,



with secular matrix

$$\mathbf{P'BP} = \begin{matrix} & \begin{matrix} \Psi(1') & \Psi(2') & \Psi(3') & \Psi(4') & \Psi(5') & \Psi(6') & \Psi(7') & \Psi(8') & \Psi(9') \end{matrix} \\ \begin{matrix} \Psi(1) \\ \Psi(2) \\ \Psi(3) \\ \Psi(4) \\ \Psi(5) \\ \Psi(6) \\ \Psi(7) \\ \Psi(8) \\ \Psi(9) \end{matrix} & \begin{bmatrix} 1 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} & 1 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{matrix} \quad \dots (7)$$

where the new normal orthogonal sequence is defined by

$$\left. \begin{aligned} \Psi(1) &= \chi(1) = \varphi(1), \\ \Psi(2) &= \chi(2) = \frac{1}{\sqrt{2}}\{\varphi(2) + \varphi(6)\}, \\ \Psi(3) &= \chi(3) = \frac{1}{\sqrt{2}}\{\varphi(3) + \varphi(7)\}, \\ \Psi(4) &= \chi(4) = \frac{1}{\sqrt{2}}\{\varphi(4) + \varphi(8)\}, \\ \Psi(5) &= \chi(5) = \frac{1}{\sqrt{2}}\{\varphi(5) + \varphi(9)\}, \\ \Psi(6) &= \chi(6) = \frac{1}{\sqrt{2}}\{\varphi(2) - \varphi(6)\}, \\ \Psi(7) &= \chi(7) = \frac{1}{\sqrt{2}}\{\varphi(3) - \varphi(7)\}, \\ \Psi(8) &= \frac{1}{\sqrt{2}}\{\chi(8) + \chi(9)\} = \frac{1}{2}\{\varphi(4) + \varphi(5) - \varphi(8) - \varphi(9)\}, \\ \Psi(9) &= \frac{1}{\sqrt{2}}\{\chi(8) - \chi(9)\} = \frac{1}{2}\{\varphi(4) - \varphi(5) - \varphi(8) + \varphi(9)\}, \end{aligned} \right\} \dots (8)$$

and similarly for  $\Psi(1'), \dots, \Psi(9')$ .

The transformation from  $\varphi$  to  $\Psi$  can be written  $\underline{\Psi} = \mathbf{P}'\underline{\varphi}$ , where  $\underline{\Psi}$  is the column with nine elements  $\Psi(1), \dots, \Psi(9)$  and  $\mathbf{P}$  is the orthogonal matrix (i.e.  $\mathbf{P}^{-1} = \mathbf{P}'$ ) obtained from (8):

$$\mathbf{P}' = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 1/2 & 1/2 & 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & 0 & 1/2 & -1/2 & 0 & 0 & -1/2 & 1/2 \end{bmatrix} \quad \dots (9)$$

That the matrix (7) is in fact  $\mathbf{P'BP}$  can be easily verified.



The eigenvalue problem

$$\mathbf{B}\mathbf{B}'\mathbf{u} = \lambda^2 \mathbf{u} \quad \dots\dots\dots (10)$$

is now transformed to

$$\mathbf{P}'\mathbf{B}\mathbf{B}'\mathbf{P}(\mathbf{P}'\mathbf{u}) = \lambda^2 (\mathbf{P}'\mathbf{u}), \quad \dots\dots\dots (11)$$

so that  $\lambda^2$  are the eigenvalues and  $\mathbf{P}'\mathbf{u}$  the eigenvectors of  $\mathbf{P}'\mathbf{B}\mathbf{B}'\mathbf{P}$ . The problem is accordingly reduced to the determination of the eigenvalues and eigenvectors of

$$\mathbf{P}'\mathbf{B}\mathbf{B}'\mathbf{P} = \begin{bmatrix} 3 & \sqrt{2} & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 2 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 1 & 1 & 0 & 0 & 0 & 0 \\ \sqrt{2} & 1 & 1 & 4 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 1 & 2 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 2 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} & \sqrt{2} & 3 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \dots\dots (12)$$

obtained from (7), using

$$\mathbf{P}'\mathbf{B}\mathbf{B}'\mathbf{P} = (\mathbf{P}'\mathbf{B}\mathbf{P})(\mathbf{P}'\mathbf{B}\mathbf{P})'.$$

To summarize the method used in this section: the symmetry of the molecule is used to write down the "split" molecule (6) from which  $\mathbf{P}'\mathbf{B}\mathbf{P}$  can be written down immediately as in (7); the transforming matrix  $\mathbf{P}$  is found most easily by carrying out the two changes of base written out in detail in (3) and (8).

#### IV. SOLUTION

The original eigenvalue problem in 18 dimensions has been reduced to three eigenvalue problems, one in 1 dimension, one in 3 dimensions, and one in 5 dimensions.

##### (a) One Dimension

From (12) one obtains immediately

$$\lambda_1^2 = 1 \quad \text{and} \quad \mathbf{P}'\mathbf{u}_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \quad \dots\dots\dots (13)$$

Hence

$$\mathbf{u}_1 = \mathbf{P}(\mathbf{P}'\mathbf{u}_1) = \frac{1}{\sqrt{8}} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ -1 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix}, \quad \dots\dots\dots (14)$$

and

$$\mathbf{v}_1 = \frac{1}{\lambda_1} \mathbf{B}' \mathbf{u}_1 = \frac{1}{\sqrt{8}} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ -1 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix}. \quad \dots\dots\dots (15)$$

The corresponding eigenvalues and eigenvectors of  $\mathbf{A}$  are recorded in Table 1, first column.

(b) *Three Dimensions*

The eigenvalues of

$$\begin{bmatrix} 2 & 0 & \sqrt{2} \\ 0 & 2 & \sqrt{2} \\ \sqrt{2} & \sqrt{2} & 3 \end{bmatrix}$$

are

$$\lambda_2^2 = 2, \quad \lambda_3^2 = \frac{1}{2}(5 + \sqrt{17}), \quad \lambda_4^2 = \frac{1}{2}(5 - \sqrt{17}),$$

and the corresponding eigenvectors

$$\frac{1}{2} \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \quad \frac{1}{\sqrt{(17 + \sqrt{17})}} \begin{bmatrix} \sqrt{2} \\ \sqrt{2} \\ \frac{1}{2}(1 + \sqrt{17}) \end{bmatrix}, \quad \frac{1}{\sqrt{(17 - \sqrt{17})}} \begin{bmatrix} \sqrt{2} \\ \sqrt{2} \\ \frac{1}{2}(1 - \sqrt{17}) \end{bmatrix}.$$

The vectors  $\mathbf{u}$  and  $\mathbf{v}$  corresponding to these can be found as in Section IV (a); the results for the matrix  $\mathbf{A}$  are in Table 1, columns 2-4.

(c) *Five Dimensions*

The algebra can be slightly simplified by subtracting 2 from each diagonal element giving

$$\begin{bmatrix} 1 & \sqrt{2} & 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ \sqrt{2} & 1 & 1 & 2 & 1 \\ 0 & 1 & 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \\ d \\ e \end{bmatrix} = \mu \begin{bmatrix} a \\ b \\ c \\ d \\ e \end{bmatrix}. \quad \dots\dots (16)$$

The eigenvectors are not altered but the eigenvalues will be decreased by 2, that is,  $\mu = \lambda^2 - 2$ . From (16)

$$\left. \begin{aligned} \sqrt{2}\mu(\mu^2 + \mu - 1)b &= (\mu^2 - 1)(\mu + 2)a, \\ \sqrt{2}(\mu^2 + \mu - 1)c &= (\mu^2 - 3)a, \\ \sqrt{2}\mu(\mu^2 + \mu - 1)d &= (\mu - 1)(\mu^3 - 4\mu - 2)a, \\ \sqrt{2}\mu(\mu^3 + \mu - 1)e &= (\mu + 1)(\mu^2 - 2)a, \end{aligned} \right\} \dots\dots (17)$$

and

$$\mu^5 - 3\mu^4 - 7\mu^3 + 5\mu^2 + 6\mu = 0. \quad \dots\dots\dots (18)$$

Hence  $\mu = 0$  is one solution, giving  $\lambda_5^2 = 2$  and the corresponding eigenvector

$$\frac{1}{\sqrt{6}} \begin{bmatrix} 0 \\ 1 \\ 1 \\ -1 \\ 1 \end{bmatrix}.$$

Hence one obtains the eigenvector of  $\mathbf{A}$  as recorded in Table 1, column 5. It is interesting to note that  $\pm\sqrt{2}$  are twofold degenerate eigenvalues of  $\mathbf{A}$  and hence any linear combination of the two eigenvectors listed would also be an eigenvector. The present method has overcome any difficulties of choice of the degenerate eigenvectors which may arise in the more direct method of calculation.

The four other solutions of (18) have been found by using Newton's method and from (17) the eigenvectors determined; the results are in Table 1, columns 6-9.

TABLE 1

MOLECULAR ORBITALS OF 3,4-BENZOPHENANTHRENE: BINDING ENERGIES AND COEFFICIENTS

$\pm 1$	$\pm\sqrt{2}$		$\pm\sqrt{\left(\frac{5}{2}+\frac{1}{2}\sqrt{17}\right)}$		$\pm\sqrt{\left(\frac{5}{2}-\frac{1}{2}\sqrt{17}\right)}$
$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \pm 1 \\ \mp 1 \\ 0 \\ 0 \\ \mp 1 \\ \pm 1 \end{bmatrix}$	$\begin{bmatrix} 0 \\ \sqrt{2} \\ -\sqrt{2} \\ 0 \\ 0 \\ -\sqrt{2} \\ \sqrt{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ \pm 1 \\ \pm 1 \\ \mp 1 \\ \mp 1 \\ \mp 1 \\ \mp 1 \\ \pm 1 \\ \pm 1 \end{bmatrix}$	$\frac{1}{\sqrt{(51+11\sqrt{17})}}$	$\begin{bmatrix} 0 \\ \sqrt{\left(\frac{5}{2}+\frac{1}{2}\sqrt{17}\right)} \\ \sqrt{\left(\frac{5}{2}+\frac{1}{2}\sqrt{17}\right)} \\ \sqrt{\left(\frac{31}{8}+\frac{7}{8}\sqrt{17}\right)} \\ \sqrt{\left(\frac{31}{8}+\frac{7}{8}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{5}{2}+\frac{1}{2}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{5}{2}+\frac{1}{2}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{31}{8}+\frac{7}{8}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{31}{8}+\frac{7}{8}\sqrt{17}\right)} \\ 0 \\ \pm 1 \\ \pm\frac{1}{2}(3+\sqrt{17}) \\ \pm\frac{1}{4}(5+\sqrt{17}) \\ \pm\frac{1}{4}(5+\sqrt{17}) \\ \mp 1 \\ \mp\frac{1}{2}(3+\sqrt{17}) \\ \mp\frac{1}{4}(5+\sqrt{17}) \\ \mp\frac{1}{4}(5+\sqrt{17}) \end{bmatrix}$	$\frac{1}{\sqrt{(51-11\sqrt{17})}}$	$\begin{bmatrix} 0 \\ \sqrt{\left(\frac{5}{2}-\frac{1}{2}\sqrt{17}\right)} \\ \sqrt{\left(\frac{5}{2}-\frac{1}{2}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{31}{8}-\frac{7}{8}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{31}{8}-\frac{7}{8}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{5}{2}-\frac{1}{2}\sqrt{17}\right)} \\ -\sqrt{\left(\frac{5}{2}-\frac{1}{2}\sqrt{17}\right)} \\ \sqrt{\left(\frac{31}{8}-\frac{7}{8}\sqrt{17}\right)} \\ \sqrt{\left(\frac{31}{8}-\frac{7}{8}\sqrt{17}\right)} \\ 0 \\ \pm 1 \\ \pm\frac{1}{2}(3-\sqrt{17}) \\ \pm\frac{1}{4}(5-\sqrt{17}) \\ \pm\frac{1}{4}(5-\sqrt{17}) \\ \mp 1 \\ \mp\frac{1}{2}(3-\sqrt{17}) \\ \mp\frac{1}{4}(5-\sqrt{17}) \\ \mp\frac{1}{4}(5-\sqrt{17}) \end{bmatrix}$

TABLE 1 (Continued)

	$\pm\sqrt{2}$	$\pm 2.50700$	$\pm 1.76941$	$\pm 1.12339$	$\pm 0.56759$
	0	0.32964	0.45202	0.35300	0.24981
	$\sqrt{2}$	0.19389	0.12374	-0.11517	-0.31701
	0	0.11696	-0.27599	0.36316	-0.16813
	$-\sqrt{2}$	0.34754	-0.09418	-0.19159	-0.01746
	$\sqrt{2}$	0.15365	-0.21792	-0.07642	0.29955
	$\sqrt{2}$	0.19389	0.12374	-0.11517	-0.31701
	0	0.11696	-0.27599	0.36316	-0.16813
	$-\sqrt{2}$	0.34754	-0.09418	-0.19159	-0.01746
	$\sqrt{2}$	0.15365	-0.21792	-0.07642	0.29955
$\frac{1}{\sqrt{24}}$	$\mp 2$	$\pm 0.40875$	$\pm 0.14902$	$\mp 0.02686$	$\pm 0.37859$
	$\pm 1$	$\pm 0.20883$	$\pm 0.32540$	$\pm 0.21171$	$\mp 0.11840$
	$\pm 1$	$\pm 0.27726$	$\mp 0.10645$	$\mp 0.34109$	$\mp 0.06153$
	$\mp 1$	$\pm 0.18528$	$\mp 0.20920$	$\pm 0.15272$	$\mp 0.32698$
	$\pm 1$	$\pm 0.10794$	$\mp 0.27914$	$\pm 0.25524$	$\pm 0.23155$
	$\pm 1$	$\pm 0.20883$	$\pm 0.32540$	$\pm 0.21171$	$\mp 0.11840$
	$\pm 1$	$\pm 0.27726$	$\mp 0.10645$	$\mp 0.34109$	$\mp 0.06153$
	$\mp 1$	$\pm 0.18528$	$\mp 0.20920$	$\pm 0.15272$	$\mp 0.32698$
	$\pm 1$	$\pm 0.10794$	$\mp 0.27914$	$\pm 0.25524$	$\pm 0.23155$

## V. CONCLUSION

The above method of calculation has illustrated in detail the simplifications introduced by making use of the alternant and symmetry properties of the molecule. The methods used are general ones and have been used for other alternant hydrocarbons. The quantities of chemical interest which can be derived from the results obtained for 3,4-benzophenanthrene will be discussed in a later paper.

## VI. REFERENCES

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 POTTS, R. B. (1953).—*J. Chem. Phys.* **21**: 758-9.

# THE BEHAVIOUR OF FLUIDS OF QUASI-SPHERICAL MOLECULES

## III. SURFACE TENSIONS

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[Manuscript received March 5, 1954]

### Summary

Theoretical surface tensions at absolute zero have been worked out for liquids whose molecules interact according to the Lennard-Jones potential

$$U = \frac{\lambda}{R^n} - \frac{\mu}{R^m}$$

taking the two sets of exponents:  $n=12$ ,  $m=6$  and  $n=28$ ,  $m=7$ .

The predicted difference between the reduced surface tensions for these two potentials is shown by the experimental surface tensions of monatomic and diatomic liquids on the one hand, and of liquids of polyatomic quasi-spherical molecules on the other hand.

## I. INTRODUCTION

It is frequently assumed that the potential energy  $U$  between a pair of simple and effectively spherical non-polar molecules can be well described by a bireciprocal formula in the intermolecular separation

$$\begin{aligned} U &= \frac{\lambda}{R^n} - \frac{\mu}{R^m} \\ &= E^* \left[ \frac{m}{n-m} \left( \frac{R^*}{R} \right)^n - \frac{n}{n-m} \left( \frac{R^*}{R} \right)^m \right], \quad n > m \geq 3, \quad \dots (1) \end{aligned}$$

where  $R$  is the distance between the centres of the molecules and  $E^*$  and  $R^*$  are molecular parameters. Following Lennard-Jones (1938) it has been customary to put  $n=12$ ,  $m=6$ , and this (12,6) potential has been the basis of many theoretical calculations of the properties of fluids. The choice of these exponents is generally considered to be as good as any other (see Faraday Society Discussion No. 15 on "The Equilibrium Properties of Solutions of Non-Electrolytes", 1953) and it is an arithmetically convenient one. But in Parts I and II of this series (Hamann and Lambert 1954*a*, 1954*b*) we showed that even if it is a good choice for the inert gas molecules, it will certainly not be for more complex, but still effectively spherical and non-polar molecules such as  $\text{SF}_6$ . A better choice for these molecules is  $n=28$ ,  $m=7$ .

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We have shown that many of the departures of fluids of polyatomic quasi-spherical molecules from the law of corresponding states may arise from the difference between these (28,7) and (12,6) potentials. In the present paper we shall consider how the surface tension of liquids may be affected by the change from a (12,6) to a (28,7) molecular interaction potential.

## II. THEORETICAL SURFACE ENERGIES AND SURFACE TENSIONS

Corner (1948) calculated the surface tension and surface energy of a Lennard-Jones and Devonshire (1937) type of liquid; that is, a liquid whose molecules interact according to the (12,6) potential

$$U = E^* \left[ \left( \frac{R^*}{R} \right)^{12} - 2 \left( \frac{R^*}{R} \right)^6 \right], \quad \dots \quad (2)$$

and are localized near the sites of a cubic close-packed lattice. For normal liquid temperatures this computation is rather laborious and not very accurate. Here we shall confine ourselves to the much simpler and comparably accurate calculation of the surface tension of a classical Lennard-Jones and Devonshire liquid at absolute zero, when, of course, it is equal to the surface energy.

The surface energy  $\Omega^\circ$ , per unit area of surface at absolute zero is

$$\Omega^\circ = \Psi - \Phi,$$

where (i)  $\Phi$  is the potential energy of  $N$  molecules at the lattice points of an infinite face-centred cubic lattice containing  $N$  molecules per volume  $V$ .  $V$  is related to the distance  $a$  between lattice points by

$$V = \frac{Na^3}{2^{\frac{1}{2}}}; \quad \dots \quad (3)$$

(ii)  $\Psi$  is the potential energy of the  $N$  molecules in a column of volume  $V$  and unit cross-sectional area, constituting part of a semi-infinite face-centred cubic lattice with a plane face at which the column terminates.

We shall assume that the lattice distance  $a$  is the same near the surface as it is in the bulk of the liquid. If we define  $\psi_l$  as the potential energy of a molecule in the  $l$ th layer of molecules ( $l=1$  for the surface layer,  $l=2$  for the second layer, . . .) then clearly

$$\Phi = N\psi_\infty.$$

If the intermolecular potential is given by (1) then

$$\psi_l = -\frac{1}{2}E^* \left[ \frac{n}{n-m} D_{m,l} \left( \frac{V_0}{V} \right)^{\frac{m}{3}} - \frac{m}{n-m} D_{n,l} \left( \frac{V_0}{V} \right)^{\frac{n}{3}} \right], \quad \dots \quad (4)$$

where

$$V_0 = \frac{NR^*{}^3}{2^{\frac{1}{2}}},$$

$$D_{s,l} = \sum_{j=1}^{\infty} n_{ij} j^{-\frac{s}{2}},$$

$n_{l,j}$  is the number of molecules in the  $j$ th shell (of radius  $j^{\frac{1}{2}}a$ ) around a molecule in the  $l$ th layer. The factor  $\frac{1}{2}$  in (4) is required to avoid counting the interaction energy between each pair of molecules twice. The numbers  $n_{l,j}$  are determined by the particular lattice face which is exposed. Corner (1948) showed that the preferred surface of a cubic close-packed liquid is the (111) face. The distribution of some of the molecules in this surface and in the layers below it is shown in Table 1.

TABLE 1  
THE NUMBERS  $n_{l,j}$

$l \backslash j$	1	2	3	4	5	6	7
1	9	3	15	9	12	4	30
2	12	6	21	9	18	7	36
3	12	6	24	12	24	7	42
> 4	12	6	24	12	24	8	48

The  $D_{s,l}$  of equation (4) are analogous to the  $C_s$  of Lennard-Jones and Ingham (1925), and, in fact

$$D_{s,\infty} = C_s.$$

Some values of  $D_{s,l}$  are given in Table 2.

TABLE 2  
 $D_{s,l}$

$s \backslash l$	1	2	3	4	$\infty$
6	10.27	13.95	14.17	14.20	14.45
7	9.74	13.17	13.28	13.29	13.36
12	9.07	12.13	12.13	12.13	12.13
28	9.00	12.00	12.00	12.00	12.00
$\infty$	9.00	12.00	12.00	12.00	12.00

The average area occupied by each molecule in a (111) plane is

$$(3^{\frac{1}{2}}/2)a^2,$$

so that the number of molecules per unit area in each layer is

$$\frac{1}{(3^{\frac{1}{2}}/2)a^2},$$

and the number,  $\nu$ , of layers in the column of  $N$  molecules is

$$\nu = (3^{\frac{1}{2}}/2)Na^2.$$

Then, writing

$$\Delta_{s,l} = D_{s,\infty} - D_{s,l},$$

we have

$$\begin{aligned} \Omega^\circ = \Psi^\circ - \Phi &= \sum_{l=1}^{\infty} \frac{1}{2} E^* \left[ \frac{n}{n-m} \Delta_{m,l} \left( \frac{V_0}{V} \right)^{\frac{m}{3}} - \frac{m}{n-m} \Delta_{n,l} \left( \frac{V_0}{V} \right)^{\frac{n}{3}} \right] \frac{1}{(3^{1/2}/2)a^2} \quad \dots (5) \\ &= \frac{E^* \kappa}{(3^{1/2}/2)a^2}, \end{aligned}$$

where

$$\kappa = \frac{1}{2(n-m)} \sum_{l=1}^{\infty} \left[ n \Delta_{m,l} \left( \frac{V_0}{V} \right)^{\frac{m}{3}} - m \Delta_{n,l} \left( \frac{V_0}{V} \right)^{\frac{n}{3}} \right].$$

### III. NUMERICAL RESULTS

In solving equation (5) it is sufficient for our purpose to limit the summation for  $D_{s,l}$  to the first seven shells around each molecule, that is, to the nearest 134 lattice points. This means that we assume that only the molecules in the surface layer and the two layers immediately below it have energies significantly different from that of a molecule in the bulk of the liquid. We shall therefore take  $D_{s,\infty}$  to be given by  $D_{s,4}$ . Table 2 shows that the maximum error introduced by this approximation is about 2 per cent.

Because the molecular parameters  $E^*$  and  $V_0$  are known for only a few substances it is desirable to express the surface energy (5) in terms of the more accessible critical temperature  $T_c$  and critical volume  $V_c/\text{g-mol}$ . Defining the reduced surface energy  $(\Omega^\circ)_r$  by

$$(\Omega^\circ)_r = \Omega^\circ V_c^{1/3} / T_c,$$

we have

$$(\Omega^\circ)_r = \frac{\kappa}{3^{1/2}} \frac{E^*}{k T_c} \left( \frac{V_c}{V_0} \right)^{1/3} \left( \frac{V_0}{V} \right)^{1/3} \frac{V_c^{1/3} k}{a^2},$$

where  $k$  is Boltzmann's constant and  $V$  is now the molar volume of the liquid. From (3)

$$(\Omega^\circ)_r = \frac{R}{N_0^{1/3}} \frac{T_0}{T_c} \left( \frac{V_c}{V_0} \right)^{1/3} \left( \frac{V_0}{V} \right)^{1/3} \frac{2^{1/3} \kappa}{3^{1/2}},$$

where  $T_0 = E^*/k$ ,  $R$  is the gas constant, and  $N_0$  is Avogadro's number.

We have previously (Hamann and Lambert 1954a, 1954b) estimated  $T_c/T_0$  and  $V_c/V_0$  for several types of interaction potential, and the only remaining quantity needed to calculate  $(\Omega^\circ)_r$  is the value of  $V/V_0$  at absolute zero. This is found by applying the condition for equilibrium

$$\frac{d\Phi}{dV} = 0.$$

The solution is

$$\frac{V_0}{V} = \left( \frac{D_{m,\infty}}{D_{n,\infty}} \right)^{\frac{3}{n-m}}$$



which gives the following values of  $V_0/V$  for the (12,6) and (28,7) potentials :

Potential	$V_0/V$ at 0 °K
(12,6)	1.092
(28,7)	1.015

The final results, using these values and the critical constants from Part II of this series, are shown in Table 3.

TABLE 3  
REDUCED SURFACE ENERGIES AT ABSOLUTE ZERO  
The units of  $(\Omega^\circ)_r$  are erg deg<sup>-1</sup> g-mol<sup>-2/3</sup>

Potential	Source of Critical Constants		
	(a)	(b)	(c)
(12,6)	3.2	3.7	4.5
(28,7)	3.7	4.7	5.3

(a)  $T_c/T_0$ ,  $V_c/V_0$  from Lennard-Jones and Devonshire's cell theory (Part II of this series, Table 3, for  $z=12$ ).

(b)  $T_c/T_0$ ,  $V_c/V_0$  from second and third virial coefficients (Part II of this series, Table 3).

(c) "Experimental" values of  $T_c/T_0$ ,  $V_c/V_0$  (Part II of this series, Table 3).

This table shows that whichever set of critical constants is used, the theoretical  $(\Omega^\circ)_r$ 's for the (28,7) potential are significantly greater than those for the (12,6) potential. This is consistent with the calculated difference in the reduced heats of evaporation of the two classes of liquids (Hamann and Lambert 1954b).

#### IV. COMPARISON WITH EXPERIMENTAL RESULTS

The hypothetical surface energies (or surface tensions) of real liquids at absolute zero can only be found by a long extrapolation from measurements made over a relatively short range of temperatures. Guggenheim (1945) has published an empirical formula which could be used for this extrapolation and he has, in fact, worked out  $(\Omega^\circ)_r$  for Ne, Ar, N<sub>2</sub>, and O<sub>2</sub>. We have preferred to fit the experimental surface tensions, by least squares, to a quadratic formula in the temperature. The results are given in Table 4.

Unfortunately carbon tetrachloride is the only liquid of quasi-spherical molecules for which a sufficient range of surface tension data exists. For this reason we have included benzene in Table 4. Although the benzene molecule does not strictly conform to our definition of a quasi-spherical molecule (Hamann and Lambert 1954a) it resembles an oblate spheroid and might be expected to show some of the properties of the quasi-spherical molecules.

The difference between  $(\Omega^\circ)_r$  for the two groups of liquids in Table 4 is seen to be very similar to the predicted difference between the values of  $(\Omega^\circ)_r$  for the (12,6) and (28,7) potentials.

TABLE 4  
REDUCED SURFACE TENSIONS EXTRAPOLATED TO ABSOLUTE  
ZERO

The units of  $(\Omega^\circ)_r$  are erg deg<sup>-1</sup> g-mol<sup>-1/2</sup>

Substance	$(\Omega^\circ)_r$ Present Work*	$(\Omega^\circ)_r$ Guggenheim (1945)
Ne	4.9	4.05
N <sub>2</sub>	4.8	4.5
O <sub>2</sub>	4.7	4.4
CO	4.9	
Cl <sub>2</sub>	4.7	
CCl <sub>4</sub>	5.3	
Benzene	5.5	

\* The surface tensions have been taken from the *International Critical Tables*; the critical constants from the review of Kobe and Lynn (1953).

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# THEORY OF ALTERNATING CURRENT POLAROGRAPHY

## I. EQUATION OF THE REVERSIBLE A.C. POLAROGRAPHIC WAVE

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[Manuscript received April 7, 1954]

### Summary

An equation for the A.C. polarographic current is derived from considerations of concentration changes produced at the dropping mercury electrode in virtue of the superposition of a small sinusoidal alternating voltage onto the direct potential, for the case of reversibly reduced inorganic ions. The equation predicts the magnitude of the A.C. polarographic current at any point on the polarogram.

### I. INTRODUCTION

Breyer and Gutmann in a series of papers (1946*a*, 1946*b*, 1947*a*, 1947*b*) developed the theoretical foundations of A.C. polarography, employing the superposition of a small sinusoidal alternating voltage upon the direct potential applied to the dropping mercury electrode. The treatment referred to an electrode which, on increasing the applied direct potential, passes from polarization through a reversible stage into a state of concentration polarization. These authors developed an equation for the dynamic capacitance. The equation contained a term " $d$ " measuring the thickness of the "A.C. active space", a term which was regarded as a constant. On this assumption it was shown that the dynamic capacitance reaches a maximum at the standard potential. It was not possible, however, to calculate the dynamic capacitance because  $d$  was indeterminate.

A modified theory was then proposed by Breyer and Hacobian (1952*a*, 1952*b*) in which  $d$  was treated as a frequency dependent variable and it was derived from theoretical considerations. With the knowledge of  $d$ , a new equation for the dynamic capacitance was obtained. It was shown that the degree of irreversibility of the electrode process could be derived from measurements of the phase angle of the superimposed alternating current.

Recently, other investigators in this field, for example, Gerischer (1950, 1951), Eucken and Weblus (1951), Gerischer and Vetter (1951), Delahay and Adams (1952), Grahame (1952), Vetter (1952*a*, 1952*b*) have attempted to examine in more detail the behaviour of an electrode in the presence of combined direct and alternating fields. In general these investigations can be regarded as extensions of the original Wien-Warburg-Krüger model (Wien 1896; Warburg 1899, 1901; Krüger 1903) of the electrode. That is to say, the electrochemical properties of the electrode are derived by applying a theoretical treatment, representing the electrode as a combination of fixed capacitors and resistors.

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Several specialized equations describing the impedance of the electrode have been set up by Grahame (1952). They contain different parameters depending on the nature of the substance undergoing electrochemical change. The experimental evaluation of these parameters is, unfortunately, difficult and rather involved. Grahame was fully aware of this when he wrote (Grahame 1952): "One must proceed on the assumption that the electrode may behave like any combination of circuit elements whatsoever. Indeed, one must go further and assume that its behaviour may not be representable at all in terms of conventional circuit elements . . ."\*

The main purpose of the present communication is to examine the properties of the dropping mercury electrode from the more general point of view of A.C. current measurements, rather than from the more specialized view of the measurement of the dynamic capacitance and phase angle as was done in the past (Breyer and Hacobian 1952a, 1952b). The latter viewpoint presupposes a plausible electrode model which can have physical significance only when comparatively simple electrode systems are considered. By dispensing with artificial models of the electrode, the fundamental equations can be derived in a more satisfactory and less ambiguous manner.

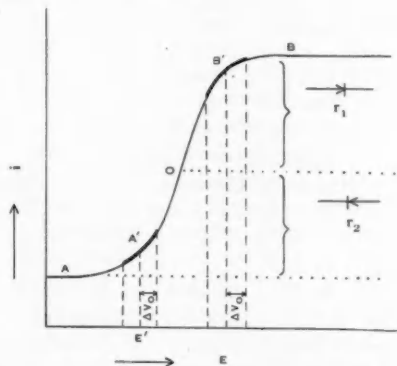


Fig. 1.—The Electrode as a non-linear element.

## II. DIFFICULTIES INVOLVED IN TRANSLATING THE PROPERTIES OF THE ELECTRODE IN TERMS OF CIRCUIT ELEMENTS

### (a) *The Electrode as a Continuously Varying Non-Linear Element*

Consider the reversible D.C. polarogram AOB (Fig. 1) where O represents the inflection point corresponding to the half-step potential ( $E_1$ ). Let a small A.C. voltage  $\Delta V$  be superimposed onto a fixed D.C. potential  $E'$  at the point A' on the polarographic curve. The electrode at this potential will behave as a non-linear element ( $r_2$ , Fig. 1) and cannot therefore be represented as any combination of fixed capacitors and resistors. At a potential corresponding to a

\* Italics by the present authors.

point  $B'$  on the curve the electrode will behave non-linearly in the opposite sense. At  $O$ , however, the electrode is instantaneously linear (at the instant when  $\Delta V = 0$ ) and thus behaves as a combination of two equal non-linear elements in opposing senses. The current-voltage relationship is linear only when the amplitude of the A.C. voltage is made vanishingly small. It is this particular condition that apparently permits a translation of the electrode into terms of a combination of fixed circuit elements. However, this picture is only approximately true, since even in this case the representative circuit fails to explain the relationship between current and frequency as predicted from theoretical considerations (e.g. Gerischer 1950, 1951; Gerischer and Vetter 1951; Grahame 1952).

#### (b) *Effect of Harmonics on Phase Angle Measurements*

The presence of harmonics, particularly odd harmonics, even in the case of a reversible electrode process, is large enough to be significant. It follows that the measurement of phase angle between A.C. current and voltage will produce difficulties, since both current and voltage are polyphase quantities.

The effect of harmonics on the r.m.s. value of the current, however, is small. Assuming the amplitude of the fundamental to be  $100 \mu\text{A}$  and that of the third and fifth harmonic components to be 25 and  $5 \mu\text{A}$  respectively, the r.m.s. value of the resultant current (neglecting higher order harmonics) is given by

$$\sqrt{\left(\frac{100^2 + 25^2 + 5^2}{2}\right)} = 72.8 \mu\text{A},$$

whereas if only the fundamental were present the r.m.s. value would be  $70.7 \mu\text{A}$ . Thus the r.m.s. current is increased by only 3 per cent., indicating that the current changes but little, even in the presence of relatively large harmonic components.

The presence of harmonics, however, greatly affects the practical determination of the faradaic impedance of the electrode when the usual null (Wheatstone bridge) method is used. In all impedance measurements involving the dropping mercury electrode, only a minimum balance and no actual null point is obtained. It is, therefore, advisable to abandon the usual electrode model in terms of capacitors and resistors and to substitute a treatment based on current measurements.

### III. SCHEMATIC REPRESENTATION OF THE ELECTRODE-SOLUTION SYSTEM

The electrode system under consideration consists of a dropping mercury electrode immersed into a solution containing a small amount of reducible substance and an excess of inert (supporting) electrolyte. A direct potential is applied to the electrode simultaneously with a sinusoidal voltage of low frequency and amplitude.

In order to derive a workable equation for the A.C. polarographic current, it is convenient to represent the electrode/solution system diagrammatically as shown in Figure 2.

In the reversible reduction of simple inorganic ions, the space within which the electrode process\* occurs can be schematically represented as being bounded by  $EE'D'D$  (Fig. 2), where  $EE'$  signifies the electrode/solution boundary. The establishment of electrochemical equilibrium is assumed to be fast compared with the rate of diffusion. Consequently the steady-state concentration of reducible substances in the region of the electrode process will be practically independent of the distance  $x$  from the electrode. The concentration gradient of the reducible substance extends thus from  $BB'$  to  $DD'$ .

The relevant regions of the electrode/solution system will now be discussed. Region I is the space bounded by the electrode/solution interface  $EE'$  and the plane of the electrical centres of the first layer of ions ( $AA'$ , Fig. 2), the outer rigid Helmholtz plane as defined by Grahame (1947). Region II is the space

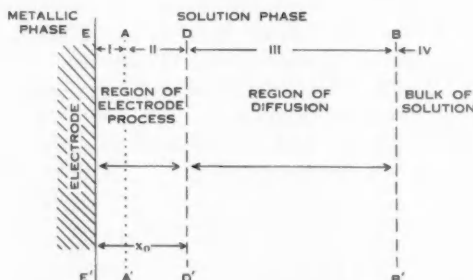


Fig. 2.—Schematic representation of the electrode/solution system in the absence of an A.C. field.

bounded by  $AA'$  and by  $DD'$ , the inner diffusion boundary. Region III, bounded by  $DD'$  and by  $BB'$ , represents the D.C. diffusion region. The bulk of the solution, not subject to diffusion forces, is represented by region IV. Region I is small compared with region II, which in turn is much smaller than region III. The electrode process can occur either in both regions I and II or in region I alone. The latter obtains in processes preceded by adsorption which will be considered separately in a later communication. For the present case the electrode process is assumed to occur in both regions I and II.

Figure 2 thus shows schematically the steady-state picture when a D.C. potential, sufficiently high to produce an electrochemical reaction, is applied to the electrode. A steady-state D.C. diffusion current flows which is mainly determined by the concentration gradient set up in region III. In other words, the D.C. polarographic current  $i$  is directly proportional to the difference between

\* By "electrode process" here is meant not only the actual electron transfer, but the sum total of all processes preceding and following it as, for example, solvation/desolvation, amalgamation/deamalgamation, adsorption/desorption of the substance undergoing the electrochemical change. Diffusion processes occurring in space III are specifically excluded from the term.

the concentration of reducible ion in the bulk  $c_B$  and that in region II,  $c_{II}$ , so that

$$i = K(c_B - c_{II}), \quad \dots \quad (1)$$

and

$$i_d = Kc_B, \quad \dots \quad (2)$$

where  $i_d$  is the limiting current and  $K$  is the Ilković constant. No changes in the charge density at the electrode surface will be observed as a result of the electrode process, once the steady state has been reached. In the presence of an A.C. field, however, variations of charge density will result at the electrode surface and consequently a movement of charged particles is established in the space near the electrode. Or in other words, a concentration wave extending from the electrode surface into the solution is now set up.

In the ordinary D.C. polarographic case it is thus sufficient to consider  $DD'$  as the electrode/solution boundary and solve the diffusion equation with the arbitrary assumption that the electrode surface and plane  $DD'$  are coincident. In the A.C. case, however, the characteristic process, which will be discussed later, takes place in regions I and II. Thus in the case of A.C. polarography, the boundary is actually the electrode/solution boundary  $EE'$ .

In the presence of a low frequency A.C. field, the concentration will vary periodically with both  $x$  and time. It will be seen in the following section that the amplitude of the concentration change diminishes with the distance  $x$  from the electrode. The alternating current  $i_{\sim}$  can thus be represented as

$$i_{\sim} = K' \cdot \Delta c_0, \quad \dots \quad (3)$$

where  $\Delta c_0$  is the concentration change at the electrode surface and  $K'$  is a constant for one and the same electrolyte.  $\Delta c_0$  is a function of time, of the amplitude of the A.C. voltage, and of the magnitude of the D.C. potential.

It can be shown experimentally that the alternating polarographic current is unaffected by the D.C. diffusion process occurring in region III. Thus, for instance, in the D.C. polarography of the  $Fe^{+++}/Fe^{++}$  system (e.g. as oxalate or citrate complex) three different types of steps are obtained depending on whether a ferric or ferrous salt solution or a mixture of both is used. The magnitude of the D.C. polarographic current at the half-step potential is (i)  $(-i_d)/2$  in the case of ferric, (ii)  $(+i_d)/2$  in the case of ferrous, and (iii) zero in the case of an equal mixture of ferric and ferrous complex ions (Fig. 3). The corresponding alternating current, however, remains unchanged. This proves that the alternating current depends only on the relative concentrations of ferric and ferrous complex ions at the electrode, and is independent of D.C. diffusion processes occurring in region III.

It is essential at this point to stress the differences between the polarographic A.C. and D.C. currents respectively. Whereas the A.C. current is the result of a reversible or almost reversible electrode reaction, occurring in regions I and II, the D.C. current includes the irreversible process of charge transport in the diffusion layer (region III, Fig. 2). In other words, the D.C. process

consists of a reversible part occurring near the electrode and an irreversible part due to diffusion. This fact seemingly invalidates the applicability of the reversible electrode equation. But Helmholtz (1878) pointed out that diffusion is to be disregarded and the second law is to be applied to that part of the total process which is reversible (i.e. to the interface reaction in our case). It is thus reasonable to suppose that the two processes, diffusion and electrode reaction,

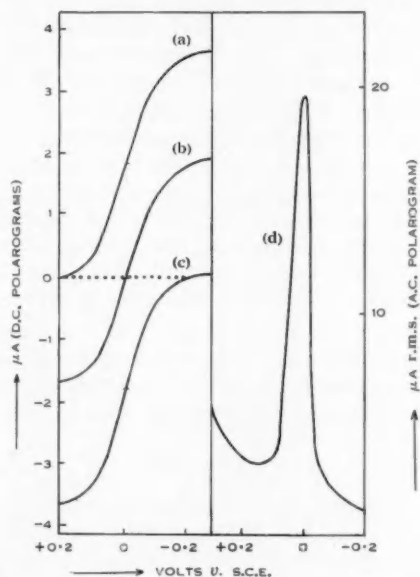


Fig. 3.—A.C. and D.C. polarograms of ferrous and ferric complex ion in 0.5M oxalic acid as supporting electrolyte (air-free). A.C. 15 mV r.m.s. Capillary characteristics:  $m$ ,  $1.1 \text{ mg sec}^{-1}$ ;  $t$ ,  $4.2 \text{ sec}$  at zero applied potential;  $T$ ,  $20^\circ \text{C}$ .

- (a) Cathodic D.C. polarogram of  $10^{-3}\text{M}$  ferric complex ion.
- (b) Combined cathodic-anodic D.C. polarogram of a mixture of  $5 \times 10^{-4}\text{M}$  ferrous and  $5 \times 10^{-4}\text{M}$  ferric ion.
- (c) Anodic D.C. polarogram of  $10^{-3}\text{M}$  ferrous complex ion.
- (d) A.C. polarogram corresponding to (a), (b), and (c).

are merely superimposed and that one may be ignored when thermodynamically considering the other.\* In the case of irreversible D.C. polarographic reductions, no equilibrium between the oxidized and reduced forms near the electrode subsists, although stationary concentrations of these substances can be established as a result of the applied D.C. potential.

\* This condition, however, only applies when the speed of establishment of electrochemical equilibrium is considerably faster than the speed of diffusion (Delahay 1953). Otherwise no stationary concentration of the reducible substance can exist near the electrode and the reversible equation cannot be applied.



It has been shown that the criterion of D.C. polarographic reversibility depends to a large extent on the magnitude of the reaction rate constants at the equilibrium potential (Eyring, Marker, and Kwoh 1949; Delahay 1951, 1953; Delahay and Strassner 1951). Since the A.C. polarographic current is a result of concentration changes set up at the electrode, it is evident that the speed of the electrode reaction must be greater than the rate of variation of the A.C. voltage. In other words, when the A.C. frequency exceeds the velocity of the electrode reaction, no concentration changes can occur and hence no A.C. wave results. In the experience of the present authors inorganic ions gave A.C. waves only when the electrode process could be termed reversible or almost reversible from the D.C. polarographic point of view, that is, when the corresponding D.C. step shows a linear log  $(i_d - i)/i$  versus  $E$  plot with the required theoretical slope or nearly so. Frankly irreversible electrode processes do not produce A.C. waves (Breyer, Gutmann, and Hacopian, 1950a, 1950b).

#### IV. EQUATION OF THE REVERSIBLE A.C. POLAROGRAPHIC WAVE

Consider the reversible electrochemical reaction



occurring at the dropping mercury electrode under specified conditions as described in Section III. Let a small, sinusoidal A.C. voltage be superimposed onto the D.C. potential  $E$ . If  $\Delta V$  signifies the instantaneous voltage and  $\Delta V_0$  the amplitude

$$\Delta V = \Delta V_0 \cos \omega \tau. \quad (5)$$

An A.C. current,  $\Delta i$  is produced according to the equation

$$\Delta i = \Delta i_0 \cos(\omega \tau + \theta) + \Delta i'_0 \cos(2\omega \tau + \theta_1) + \Delta i''_0 \cos(3\omega \tau + \theta_2) + \dots, \quad (6)$$

where  $\Delta i_0$ ,  $\Delta i'_0$ , and  $\Delta i''_0 \dots$  are the amplitudes of the fundamental, second, third, . . . etc. harmonics respectively and  $\theta$ ,  $\theta_1$ ,  $\theta_2$ , . . . the corresponding phase angles. This current flows in addition to the direct current,  $i$ . Hence the total current  $i_t$  is given by

$$i_t = i + \Delta i. \quad (7)$$

Variations in concentration (activity) close to the electrode surface will occur and such variations will be a function of the distance from the electrode surface  $x$ , the time  $\tau$ , and the applied D.C. potential  $E$ . These variations are determined by the relationship

$$\Delta c_{(x,\tau,E)} = \Delta c_{0(x,E)} \cos(\omega \tau + \theta') + \Delta c'_{0(x,E)} \cos(2\omega \tau + \theta'_1) + \Delta c''_{0(x,E)} \cos(3\omega \tau + \theta'_2) + \dots, \quad (8)$$

where  $\Delta c_{0(x,E)}$ ,  $\Delta c'_{0(x,E)}$ , and  $\Delta c''_{0(x,E)}$  are the amplitudes of the fundamental, second, and third . . . harmonics and  $\theta'$ ,  $\theta'_1$ ,  $\theta'_2$  the corresponding phase angles of the concentration change relative to the applied A.C. voltage. The concentration of the reducible substance in spaces I and II ( $c_{(0,E)}$ ) in the absence of an A.C.

field is assumed to be independent of  $x$  (cf. Section III) hence the instantaneous concentration  $c_{(x,\tau,E)}$  is given by

$$c_{(x,\tau,E)} = c_{(0,E)} + \Delta c_{(x,\tau,E)}, \quad (9)$$

By combining equation (9) with the expression for linear diffusion at a plane electrode

$$\frac{\partial c_{(x,\tau,E)}}{\partial \tau} - D \frac{\partial^2 c_{(x,\tau,E)}}{\partial x^2} = 0, \quad (10)$$

( $D$  = diffusion coefficient of the reducible ion) the following relationship is obtained

$$\frac{\partial \Delta c_{(x,\tau,E)}}{\partial \tau} - D \frac{\partial^2 \Delta c_{(x,\tau,E)}}{\partial x^2} = 0. \quad (11)$$

Solving (9) and (11) for the steady state the following equation can be derived by means of the Laplace transformation method (Carslaw and Jaeger 1947)

$$\begin{aligned} \Delta c_{(x,\tau,E)} = & \Delta c_{0(x,E)} e^{-\sqrt{(\omega/2D)} \cdot x} \cos(\omega\tau - \sqrt{(\omega/2D)} \cdot x + \theta') \\ & + \Delta c'_{0(x,E)} e^{-\sqrt{(\omega/D)} \cdot x} \cos(2\omega\tau - \sqrt{(\omega/D)} \cdot x + \theta'_1) \\ & + \Delta c''_{0(x,E)} e^{-\sqrt{(3\omega/2D)} \cdot x} \cos(3\omega\tau - \sqrt{(3\omega/2D)} \cdot x + \theta'_2) + \dots * \quad (12) \end{aligned}$$

For the boundary condition ( $x=0$ )

$$\frac{\partial \Delta c_{(0,\tau,E)}}{\partial x_{x=0}} = \sum_{l=1}^{l=n} -\Delta c_0^l \sqrt{\left(\frac{l\omega}{D}\right)} \cos\left(l\omega\tau + \theta' + \frac{\pi}{4}\right), \quad (13)$$

when the amplitudes of the harmonics are small compared to that of the fundamental, all terms containing  $l\omega$  ( $l > 1$ ) can be neglected and the equation reduces to

$$\frac{\partial (\Delta c_{(0,\tau,E)})}{\partial x_{x=0}} = -\Delta c_{0(0,E)} \sqrt{\left(\frac{\omega}{D}\right)} \cos\left(\omega\tau + \theta' + \frac{\pi}{4}\right), \quad (14)$$

which is the solution obtained by Randles (1947). The same solution is obtained by solving equations (9) and (11) without the use of the Laplace transform method (cf. Appendix I).

The alternating current  $\Delta i_{(E)}$  corresponding to the applied D.C. potential  $E$  is expressed as

$$\Delta i_{(E)} = -nFA \text{ flux},$$

in which

$$\text{flux} = D \frac{\partial (\Delta c_{(0,\tau,E)})}{\partial x_{x \rightarrow 0}};$$

that is

$$\Delta i_{(E)} = -nFAD \frac{\partial (\Delta c_{(0,\tau,E)})}{\partial x_{x \rightarrow 0}}, \quad (15)$$

where

$$A = b(mt)^{2/3}. \quad (16)$$

\* The solution is obtained by drawing an analogy between the conduction of heat in an isotropic solid (heat transfer) and the diffusion of particles in a liquid as in our case (mass transfer) (see, for example, Randles 1947).

$A$  denotes the area of the electrode surface;  $b$  ( $=8.5 \times 10^{-1}$ ) has the dimensions  $M^{-2/3}L^2$  and involves the specific gravity of mercury;  $m$  is the mass of mercury flowing from the capillary ( $g \text{ sec}^{-1}$ );  $t$  is the capillary drop time in seconds;  $n$  and  $F$  have their usual meaning. Combining (14) and (15) we obtain the expression

$$\Delta i_{(E)} = nFA\Delta c_{0(0,E)} \sqrt{(\omega D)} \cos(\omega\tau + \theta' + \pi/4). \quad (17)$$

The amplitude of the alternating current is therefore given by

$$\Delta i_{0(E)} = nFA\Delta c_{0(0,E)} \sqrt{(\omega D)}, \quad (18)$$

in which

$$\theta = \theta' + \pi/4. \quad (19)$$

It is evident from equation (18) that the amplitude of the A.C. current is directly proportional to the peak of the concentration change  $\Delta c_{0(0,E)}$  at the electrode.

The relationship between concentration change and total applied potential is given by

$$E + \Delta V_0 \cos \omega\tau = E_1 + \frac{RT}{nF} \ln \frac{c_{(x_0,E)} + \Delta c_{0(x_0,E)} \cos(\omega\tau + \theta')}{[c_B - c_{(x_0,E)}] - \Delta c_{0(x_0,E)} \cos(\omega\tau + \theta')}, \quad (20)$$

where  $c_{(x_0,E)}$  represents the concentration of the reducible ion at the distance  $x_0$  from the plane electrode (cf. Fig. 2),  $c_B$  the bulk concentration, and  $x_0$  the distance of the plane  $DD'$  from the electrode.

From the reversible D.C. polarographic equation

$$\frac{c_{\text{Ox}}^{\text{cl}}(E)}{c_{\text{Red}}^{\text{cl}}(E)} = \frac{c_{(x_0,E)}}{c_B - c_{(x_0,E)}} = e^{nF\Delta E/RT} = e^\psi, \quad (21)$$

in which  $c_{\text{Ox}}^{\text{cl}}(E)$  = concentration of reducible particles at the electrode,

$c_{\text{Red}}^{\text{cl}}(E)$  = concentration of reduced particles at the electrode,

$c_{(x_0,E)}$  = concentration of reducible particles distant  $x_0$  from the electrode,

$$\psi = \psi(E) = \frac{nF\Delta E}{RT},$$

$$\Delta E = E - E_1,$$

$c_{\text{Ox}}^{\text{cl}}(E)$  is equal to  $c_{(x_0,E)}$  because in the case of a reversible electrode process the steady-state concentration in regions I and II (Fig. 2) in the absence of alternating current is assumed to be independent of  $x$  (Section III).

Rearranging (21) we obtain the expressions

$$c_{(x_0,E)} = \left( \frac{e^\psi}{1 + e^\psi} \right) c_B, \quad (22)$$

and

$$c_B - c_{(x_0,E)} = \left( \frac{1}{1 + e^\psi} \right) c_B. \quad (23)$$

Substituting (22) and (23) into (20)

$$E + \Delta V_0 \cos \omega \tau = E_i + \frac{RT}{nF} \ln \frac{[e^{\psi}/(1+e^{\psi})]c_B + \Delta c_{0(x_0, E)} \cos(\omega \tau + \theta')}{[1/(1+e^{\psi})]c_B - \Delta c_{0(x_0, E)} \cos(\omega \tau + \theta')}, \quad \dots (24)$$

and rearranging

$$e^{\varphi} = \frac{[e^{\psi}/(1+e^{\psi})]c_B + \Delta c_{0(x_0, E)} \cos(\omega \tau + \theta')}{[1/(1+e^{\psi})]c_B - \Delta c_{0(x_0, E)} \cos(\omega \tau + \theta')}, \quad \dots (25)$$

where

$$\varphi = \varphi_{(E, \tau)} = \frac{nF(\Delta E + \Delta V_0 \cos \omega \tau)}{RT}. \quad \dots (26)$$

Having in mind that for a reversible process concentration changes and A.C. voltage are in phase, that is,  $\theta' = 0$ , and rearranging (25) we obtain the expression

$$\Delta c_{0(x_0, E)} \cos \omega \tau = c_B \frac{(e^{\varphi} - e^{\psi})}{(1+e^{\psi})(e^{\varphi} + 1)}, \quad \dots (27)$$

at  $\tau = 0$

$$\Delta c_{0(x_0, E)} = \frac{c_B(e^{\varphi_0} - e^{\psi})}{(1+e^{\psi})(e^{\varphi_0} + 1)}, \quad \dots (28)$$

where

$$\varphi_0 = \frac{nF(\Delta E + \Delta V_0)}{RT} = \psi + \frac{nF\Delta V_0}{RT}, \quad \dots (29)$$

or

$$\varphi_0 = \psi + \lambda, \quad \dots (30)$$

where

$$\lambda = \frac{nF\Delta V_0}{RT}. \quad \dots (31)$$

Equation (28) can now be written as

$$\Delta c_{0(x_0, E)} = \frac{c_B(e^{\psi + \lambda} - e^{\psi})}{(1+e^{\psi})(e^{\psi + \lambda} + 1)}, \quad \dots (32)$$

or

$$\Delta c_{0(x_0, E)} = \frac{c_B(e^{\lambda} - 1)}{(e^{\lambda} + e^{-\psi})(1+e^{\psi})}, \quad \dots (33)$$

and equating

$$e^{\lambda} = K, \quad \dots (34)$$

$$\Delta c_{0(x_0, E)} = \frac{c_B(K - 1)}{(K + 1) + (K e^{\psi} + e^{-\psi})}. \quad \dots (35)$$

Now,  $K e^{\psi} + e^{-\psi}$  is always greater than 0 (i.e. it is always positive) for all values of  $\psi$  (+ve or -ve). For small values of  $\Delta V_0$ , equation (35) reaches a maximum value for  $\psi = 0$ , that is, when  $\Delta E = 0$  or  $E = E_i = E_s$ . Thus a maximum concentration change occurs when the applied D.C. potential corresponds to the half-step or summit potential and equation (35) reduces to

$$\begin{aligned} \Delta c_{0(x_0, E_s)} &= \frac{c_B(K - 1)}{2(K + 1)} \\ &= \frac{c_B}{2} \tanh \left( \frac{nF\Delta V_0}{2RT} \right). \quad \dots (36) \end{aligned}$$

This expression is identical with that obtained when equation (14) of a previous paper (Breyer and Hacopian 1952*a*) is applied to the reversible case.

Equations (35) and (36) express  $\Delta c_{0(x_0, E)}$  in terms of the bulk concentration of the reducible ion. Since  $\Delta c_{0(0, E)}$  is always greater than  $\Delta c_{0(x_0, E)}$  we can write

$$\Delta c_{0(0, E)} = p \Delta c_{0(x_0, E)}, \quad \dots \dots \dots (37)$$

where  $p > 1$ ,  $p$  being a dimensionless factor depending on the structure of the electrical double layer and the nature of supporting electrolyte.\*

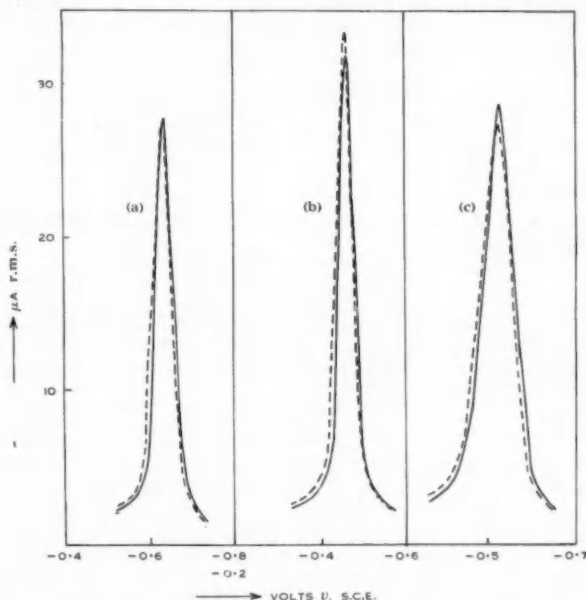


Fig. 4.—Comparison between observed and calculated A.C. polarograms of (a)  $10^{-3}\text{N Cd}^{++}$ , (b)  $10^{-3}\text{N Pb}^{++}$ , and (c)  $10^{-3}\text{N Tl}^{+}$  in  $0.5\text{N HCl}$  (air-free). A.C.  $15\text{ mV r.m.s.}$ ;  $T, 20^{\circ}\text{C}$ . Capillary characteristics as those in Figure 3.

----- Observed polarographic curve.  
 ———— Calculated curve.

Substituting (36) and (37) in equation (17)

$$\Delta i_{(E)} = nFA \sqrt{(\omega D)} c_B \frac{(K-1)}{(K+1) + (Ke^{\psi} + e^{-\psi})} \cdot \cos \left( \omega \tau + \theta' + \frac{\pi}{4} \right), \quad \dots (38)$$

\* Experimental work has shown, however, that  $p > 1$  only at high concentrations of supporting electrolyte. In strong electrolytes up to a concentration of  $0.5\text{N}$   $p=1$ .

where  $\Delta i_{(E)}$  signifies the instantaneous A.C. polarographic current corresponding to the applied D.C. potential  $E$ . The amplitude of this current is given by

$$\Delta i_{0(E)} = nFA \sqrt{(\omega D)} c_B \frac{(K-1)}{(K+1) + (Ke\psi + e^{-\psi})}, \quad \dots (39)$$

and at the summit potential by

$$\Delta i_{0(E_p)} = \frac{nFA \sqrt{(\omega D)}}{2} \cdot c_B \cdot \tanh \left( \frac{nF\Delta V_0}{2RT} \right). \quad \dots (40)$$

Substituting the capillary characteristics for the electrode area  $A$  (cf. equation (16)), the r.m.s. current at any point of the A.C. polarographic wave is expressed as

$$\Delta i_{(E)r.m.s.} = \frac{nb(mt)^{2/3} F(\omega D)^{1/2} c_B [\exp(nF\Delta V_0/RT) - 1]}{\sqrt{2} \left[ \exp\left(\frac{nF\Delta V_0}{RT}\right) + \exp\left(\frac{nF\Delta E + \Delta V_0}{RT}\right) + \exp\left(\frac{-nF\Delta E}{RT}\right) + 1 \right]}. \quad \dots (41)$$

The validity of this equation has been tested experimentally. The results are shown in Figure 4.

#### V. ACKNOWLEDGMENTS

The authors wish to thank the Trustees of the Science and Industry Endowment Fund for financial assistance. Thanks are also due to Mr. H. H. Bauer for checking parts of the manuscript and to Miss M. Ford for carrying out some of the experimental work.

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## APPENDIX I

*Solution of Equations (9) and (11) without the Use of the Laplace Transform*

Although the solution is not rigorous, it gives the same result as that shown by equation (12) in the text. Neglecting higher harmonics equation (8) reduces to

$$\Delta c_{(x,\tau,E)} = \Delta c_{0(x,E)} \cos(\omega\tau + \theta') \quad \dots\dots\dots (42)$$

$$= \Delta c_{0(x,E)} \operatorname{Re} e^{i(\omega\tau + \theta')}, \quad \dots\dots\dots (43)$$

where R signifies the real part and  $i = \sqrt{-1}$ . Thus equation (9) becomes

$$c_{(x,\tau,E)} = c_{(0,E)} + \Delta c_{0(x,E)} \operatorname{Re} e^{i(\omega\tau + \theta')}, \quad \dots\dots\dots (44)$$

and substituting (44) in equation (10) we obtain

$$\frac{\partial [\Delta c_{0(x,E)} \operatorname{Re} e^{i(\omega\tau + \theta')}] }{\partial \tau} - D \frac{\partial^2 [\Delta c_{0(x,E)} \operatorname{Re} e^{i(\omega\tau + \theta')}] }{\partial x^2} = 0. \quad \dots\dots\dots (45)$$

In order to solve (44) and (10) we first must obtain the solution of

$$c_{(x,\tau,E)} = c_{(0,E)} + \Delta c_{0(x,E)} e^{i(\omega\tau + \theta')}, \quad \dots\dots\dots (46)$$

and of equation (10). Substituting (46) in (10)

$$\frac{\partial [\Delta c_{0(x,E)} e^{i(\omega\tau + \theta')}] }{\partial \tau} - D \frac{\partial^2 [\Delta c_{0(x,E)} e^{i(\omega\tau + \theta')}] }{\partial x^2} = 0, \quad \dots\dots\dots (47)$$

that is,

$$\frac{d^2(\Delta c_{0(x,E)})}{dx^2} - \frac{i\omega}{D} \Delta c_{0(x,E)} = 0, \quad \dots\dots\dots (48)$$

or

$$\begin{aligned} \Delta c_{0(x,E)} &= B_1 e^{\sqrt{(i\omega/D)} \cdot x} + B_2 e^{-\sqrt{(i\omega/D)} \cdot x} \\ &= B_1 e^{(1+i)\sqrt{(\omega/2D)} \cdot x} + B_2 e^{-(1+i)\sqrt{(\omega/2D)} \cdot x}, \quad \dots\dots\dots (49) \end{aligned}$$

in which  $B_1$  and  $B_2$  are constants. This is the steady periodic solution which gives the concentration at all times after the transient disturbance caused by starting the A.C. voltage has ceased. Since  $\Delta c_0 \rightarrow 0$  as  $x \rightarrow \infty$  and since  $x$  is always positive,  $B_1$  can be assumed to be zero.

$$\Delta c_{0(x,E)} = B_2 e^{-(1+i)\sqrt{(\omega/2D)} \cdot x}, \quad \dots\dots\dots (50)$$

and from equation (42)

$$\begin{aligned} \Delta c_{(x,\tau,E)} &= R B_2 e^{-(1+i)\sqrt{(\omega/2D)} \cdot x} \cdot e^{i(\omega\tau + \theta')} \\ &= B_2 e^{-\sqrt{(\omega/2D)} \cdot x} \operatorname{Re} e^{i(\omega\tau - \sqrt{(\omega/2D)} \cdot x + \theta')} \quad \dots\dots\dots (51) \end{aligned}$$

$$= B_2 e^{-\sqrt{(\omega/2D)} \cdot x} \cos(\omega\tau - \sqrt{(\omega/2D)} \cdot x + \theta'). \quad \dots\dots\dots (52)$$

At  $x=0$

$$\Delta c_{(0,\tau,E)} = B_2 \cos (\omega \tau + \theta'). \quad \dots\dots\dots (53)$$

Comparing (53) and (42) for values of  $x=0$ , we see that  $B_2 = \Delta c_{(0,0,E)}$  and thus equation (52) becomes

$$\Delta c_{(x,\tau,E)} = \Delta c_{(0,0,E)} e^{-\sqrt{(\omega/2D)} \cdot x} \cos (\omega \tau - \sqrt{(\omega/2D)} \cdot x + \theta'), \quad \dots (54)$$

which is identical with equation (12) when higher harmonics are neglected.



# DIRECT CURRENT POLAROGRAPHY IN THE PRESENCE OF ALTERNATING VOLTAGES

## I. REVERSIBLE SYSTEMS

By G. S. BUCHANAN\* and R. L. WERNER\*

[Manuscript received March 9, 1954]

### Summary

The effect of a small sinusoidal A.C. voltage (c. 100 mV) on D.C. polarographic waves has been investigated. It has been found that the alternating current is rectified and the significance of this rectification is discussed for the case of reversibly discharged inorganic cations. A qualitative and quantitative treatment is given.

## I. INTRODUCTION

Several methods have been proposed from time to time for the investigation of irreversible systems at the dropping mercury electrode (D.M.E.). It was thought worth while to investigate the effect on D.C. polarograms of an applied A.C. voltage, in the hope that this might yield information on these processes. Significant differences have been found between reversible and irreversible systems as a result of this investigation and it is the purpose of the present and subsequent papers to present the results. This paper is concerned with reversible systems only.

## II. APPARATUS AND METHOD

The circuit shown in Figure 1 consists of the usual apparatus for D.C. polarography, but includes a 100 $\Omega$  resistor across which an A.C. voltage may be superimposed on the D.C. voltage by means of the switch *S*, as required. The source of sinusoidal A.C. was a Dawe Instruments Ltd. type 400C wide range oscillator variable from 0.1 to 1000 c/s, and for the higher frequencies a British Physical Laboratories model Lo 63A, of frequency range 50 to 55,000 c/s. The fine adjustment of A.C. voltage was made by a control on the oscillators and a vacuum tube voltmeter (V.T.V.M.) was used to measure the A.C. voltage injected into the circuit. The purpose of the 1 $\mu$ F condenser *C* was to prevent D.C. voltages being supplied from the output stages of the oscillators.

It has been shown by Breyer, Gutmann, and Hacopian (1950) in their work on A.C. polarography that the ohmic resistance of the circuit and cell must be kept low (less than c. 200 $\Omega$ ), otherwise the A.C. polarograms are distorted. This is due to the fact that the A.C. impedance of the cell is less than the D.C. impedance; it is comparable in fact to the impedance of the other circuit components. The A.C. current flowing is, therefore, a function not only of the cell process but of the remainder of the circuit. In order to lower the impedance

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of the circuit to alternating current the various higher impedance components were bypassed with electrolytic condensers, the galvanometer by  $100\mu\text{F}$  and the calomel cell by  $2000\mu\text{F}$  in the manner described by Breyer, Gutmann, and Hacopian (1951). Bypassing the slidewire *A* in this fashion was not necessary, due to its low resistance.

The experimental procedure was as follows: An A.C. voltage and frequency were selected and a D.C. voltage set on the slidewire *A* with the switch *S* open. The D.C. current was then measured on the galvanometer *G*. The switch *S* was then closed and the new D.C. current measured on *G*. The switch *S* was then opened, a new D.C. voltage 20 mV higher set on the slidewire, and the

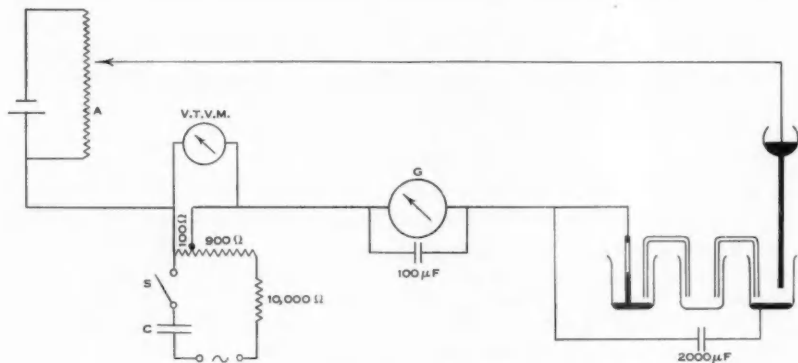


Fig. 1.—Schematic diagram of D.C. polarograph.

above procedure repeated. Thus D.C. polarograms were determined with and without alternating current flowing in the circuit. The type of wave obtained for a reversible process is shown in Figure 2. In both cases the peak readings on the galvanometer were taken.

### III. RESULTS

For simplicity we shall refer to the normal polarographic wave as the *Y* wave, and the corresponding wave produced with alternating current flowing in the current as the *Z* wave.

In Figure 2 are shown the *Y* and *Z* waves for  $1.0 \times 10^{-3} \text{M Cd}^{++}$  in  $1.0 \text{M KNO}_3$  solution (air-free) at different frequencies and 100 mV r.m.s. It can be clearly seen that the *Y* and *Z* waves cross. This occurs at the half-wave potential  $E_{\frac{1}{2}}$  in the case of these waves, and similar results are obtained in the case of lead and other reversibly reduced inorganic cations. It will be observed also, that the diffusion currents are unaffected by the presence of the alternating current.

It appeared likely that this effect had been noticed by previous workers. A careful study of the literature, however, revealed only one reference. Fournier (1952), in connection with oscillographic polarography, apparently observed a

similar phenomenon, but failed to realize its full significance and did not pursue the subject.

The qualitative explanation of these waves is simple. Consider the point  $x$  in Figure 2 (a). The  $Z$  wave starts before the  $Y$  wave due to the fact that as the A.C. voltage increases negatively,  $\text{Cd}^{++}$  ions are discharged and redissolved as the negative cycle of the alternating current decreases to zero. Since at this particular applied D.C. voltage there would normally be no discharged  $\text{Cd}^{++}$  ions in the mercury drop, there can be no A.C. current flowing on the positive sweep of the A.C. voltage. (Except that which may flow capacitatively, which however, does not register on the galvanometer.) Thus the D.C. voltage produced by rectification of the alternating current at this point causes the

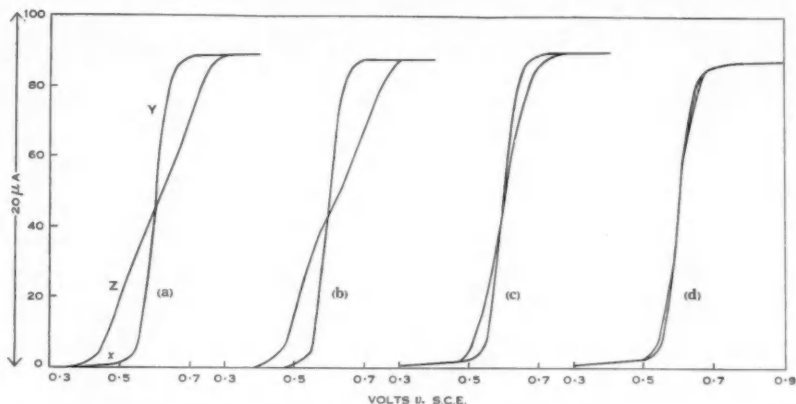


Fig. 2.— $Y$  and  $Z$  curves for  $1 \times 10^{-3} \text{M}$   $\text{Cd}^{++}$  in  $1.0 \text{M}$   $\text{KNO}_3$  (air-free).  $m = 2.56 \text{ mg sec}^{-1}$ ,  $t = 3.47 \text{ sec}$  at  $-0.7 \text{ V}$ , D.C.;  $m = 2.66 \text{ mg sec}^{-1}$ ,  $t = 3.43 \text{ sec}$  at  $-0.7 \text{ V}$ , D.C. and  $100 \text{ mV}$ , A.C. A "pool condenser" saturated calomel electrode (S.C.E.) was used as reference half-cell.

(a) 60 c/s, (b) 300 c/s, (c) 2000 c/s, (d) 5000 c/s.

electrode to behave as if it were at a more negative potential than that indicated on the slidewire  $A$ . If, however, a point is chosen on the  $Y$  curve at which the number of  $\text{Cd}^{++}$  ions in solution in the interfacial layer equals the number of  $\text{Cd}$  atoms in the mercury in the interfacial layer, and if there be no hindrance to their movement as might be expected if the process be reversible, then the positive and negative sweeps of the A.C. voltage will produce equal currents in the positive and negative directions. That is, no unidirectional current will flow, except that due to the D.C. voltage applied from  $A$ , and the  $Y$  and  $Z$  curves will coincide. As might be expected this will occur at the half-wave potential in the reversible case. Above the  $E_{\frac{1}{2}}$  value the relative concentrations of ions in the solution and the atoms in the metal at the interface results in a rectified A.C. current flow in the opposite sense to that below the  $E_{\frac{1}{2}}$  value.

The effect is essentially that of rectification of the alternating current and the addition and subtraction of the direct current thus produced to the direct current already flowing due to the D.C. voltage applied from the slidewire



still more negative potentials the alternating voltage has no effect since the process is diffusion controlled and the diffusion current is independent of the voltage.

Experimental waves obtained over a range of sweep voltages show an anticipated increase in the separation of the Y and Z waves as the sweep voltage increases. It was found that a 100 mV, r.m.s. gave a convenient separation. Too high a sweep voltage ( $>250$  mV) appeared to cause irregularities in dropping.

The influence of frequency is shown in Figure 2. Increased frequency causes a gradual diminution of separation. Below 400 cycles the change between different frequencies is negligible but then a gradual decrease in the separation of the curves occurs and the effect has practically disappeared at 5000 cycles.

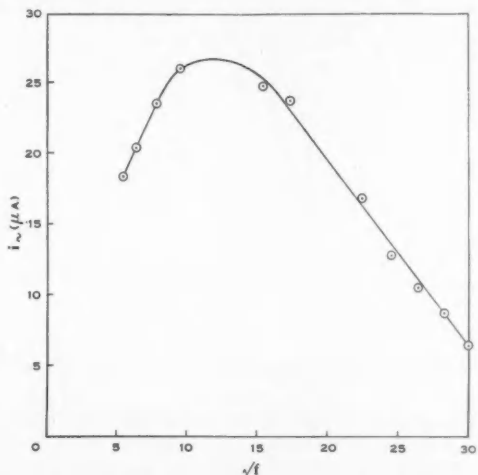


Fig. 3.—Values of A.C. peak heights for  $1.0 \times 10^{-3}M$   $Cd^{++}$  in 0.5N HCl (air-free) showing the effect of frequency on peak height.  $m=2.66$  mg sec $^{-1}$ ,  $t=3.43$  sec at 0.7 V, D.C.

It is interesting to compare this effect with influence of increasing frequency on the peak height in A.C. polarography. Figure 3 shows the effect of frequency changes on the peak heights of  $1.0 \times 10^{-3}M$   $Cd^{++}$  ion in 0.5N HCl.

The maximum occurring in the variation of A.C. peak height with frequency has not previously been reported. Randles (1947), Breyer and Hacopian (1952), and Delahay and Adams (1952) have published results showing the A.C. current and dynamic capacitance as a linearly increasing function of the square root of the frequency. If the measurements are continued at higher frequencies however, it is found that the A.C. peak heights decrease again and eventually disappear. Dr. B. Breyer (personal communication) has observed a similar effect and indeed the tendency to level out and decrease is revealed in the curves of Delahay and Adams at the highest frequencies reported by them.

It is obvious that both the A.C. polarograms and our effect diminish at approximately the same rate which presumably is due to the failure of the ions to follow the reversal of the field:

The rectification phenomenon can be quantitatively interpreted in the manner usually employed for rectifiers whose characteristic is known. In this case the characteristic of the rectifier is

$$i = \frac{i_d}{1 + e^{nF/RT(E-E_1)}}, \quad \dots \quad (1)$$

obtained by manipulation of the equation

$$E = E_1 + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right), \quad \dots \quad (2)$$

for the reversible polarographic wave. The symbols have their usual significance.

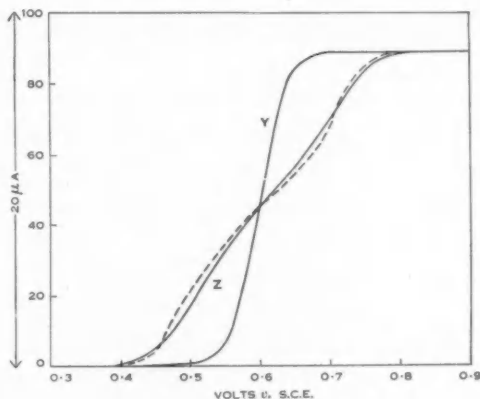


Fig. 4.—Y, Z, and theoretical waves (dashed line) for  $1 \times 10^{-3}M$   $Cd^{++}$  in  $1.0M$   $KNO_3$  (air-free). A.C. is 60 c/s at 100 mV. Other characteristics similar to Figure 2.

If the voltage consists of a steady D.C. voltage  $E$  on which is superimposed a sinusoidal voltage of frequency  $f$  and amplitude  $\varepsilon$  then the corresponding instantaneous current is given by

$$i = \frac{i_d}{1 + e^{(nF/RT)(E-E_1 + \varepsilon \sin 2\pi ft)}}, \quad \dots \quad (3)$$

and the corresponding mean current given by

$$\bar{i} = \frac{1}{T} \int_0^T \frac{i_d}{1 + e^{(nF/RT)(E-E_1 + \varepsilon \sin 2\pi ft)}} \cdot dt. \quad \dots \quad (4)$$

This equation was numerically integrated and the ratio of mean current to diffusion current evaluated for  $E-E_1$  up to  $\pm 200$  mV for a sine wave of 60 c/s

and peak amplitude 141 mV (i.e. 100 mV r.m.s.). These values are given in Table 1 and have been used to calculate the mean current in the case of a  $1.0 \times 10^{-2} \text{M Cd}^{++}$  in  $1.0 \text{M KNO}_3$  solution. In Figure 4 the experimental and calculated waves are compared. The agreement is close and the points of inflection are reproduced by the experimental wave.

TABLE 1  
VALUES OF  $\bar{i}/i_d$  FOR  $E-E_{\frac{1}{2}}$  UP TO  $\pm 200 \text{ mV}$  FOR A SINE WAVE OF 60 c/s AND  
PEAK AMPLITUDES 141 mV DERIVED FROM EQUATION (4)

$E-E_{\frac{1}{2}}$	$\bar{i}/i_d$	$E-E_{\frac{1}{2}}$	$\bar{i}/i_d$
+0.200	0.003	-0.050	0.611
+0.150	0.046	-0.100	0.759
+0.100	0.241	-0.150	0.954
+0.050	0.389	-0.200	0.997
0.000	0.500		

#### IV. CONCLUSION

The influence of an applied A.C. voltage on reversible D.C. polarograms has been investigated and the results interpreted qualitatively and quantitatively in terms of simple ionic processes. In a further paper irreversible systems will be considered.

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# CHARGE DENSITIES AND SURFACE CONDUCTANCES AT SOLID-SOLUTION INTERFACES

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[Manuscript received January 12, 1954]

## Summary

Surface charge densities for the minerals quartz ( $\text{SiO}_2$ ), corundum ( $\text{Al}_2\text{O}_3$ ), rutile ( $\text{TiO}_2$ ), cassiterite ( $\text{SnO}_2$ ), and haematite ( $\text{Fe}_2\text{O}_3$ ) have been calculated using an equation based on the kinetic theory of the diffuse layer, and requiring a knowledge of  $\zeta$ -potentials. In addition, an equation, which avoids the difficulties of earlier expressions of the kind, has been derived enabling calculation of surface charge densities from surface conductances. Values obtained from the second equation for  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ , and  $\text{TiO}_2$  were much in excess of those calculated from  $\zeta$ -potentials. The discrepancies have been attributed to considerable contribution of solid conductance to the measured surface conductance. Equations have also been derived permitting calculation of quantities characteristic of the physical properties of the porous plug packings used in the investigations.

## I. INTRODUCTION

The results of streaming potential experiments are usually expressed in terms of  $\zeta$ -potentials calculated from the Helmholtz-Smoluchowski equation

$$\zeta = -\frac{4\pi\eta EK'}{DP}, \dots\dots\dots (1)$$

where  $\eta$  = coefficient of viscosity in the diffuse layer,

$E$  = streaming potential produced between the ends of the capillary or porous plug packing,

$K'$  = specific conductivity of the liquid contained in the capillary or porous plug,

$D$  = dielectric constant of the liquid in the diffuse layer, and

$P$  = pressure producing the liquid flow.

$K'$  includes the surface conductance, that is, the additional conductance due to the ions of the electrical double layer. Although several authors (Urban and White 1932; McBain and Foster 1935; Fricke and Curtis 1936) suggest that ions of both compact and diffuse layers contribute to the surface conductance, it is not unreasonable to suppose that those in the compact layer will have much reduced mobilities, and consequently make only a small contribution to the conductance.

Useful information on the surface reactions of sparingly soluble inorganic solids has emerged from a qualitative interpretation, in terms of ion exchange or preferential ion adsorption, of the variation of  $\zeta$ -potential with electrolyte

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concentration (O'Connor and Buchanan 1953). In this method it is implicitly assumed that variation of charge density is the major factor contributing to change in  $\zeta$ -potential, and that variation in diffuse layer thickness does not alter the  $\zeta$ -potential to an appreciable extent over the concentration range usually investigated ( $2 \times 10^{-6}$  to  $1 \times 10^{-4}$  equiv/l). However, it is also desirable to have a means of calculating surface charge densities from the experimentally determinable quantities, namely, stream potential and surface conductance. Two methods appeared to be available for this purpose:

(i) An equation based upon the Debye-Hückel theory of ion distribution around a single charged particle (see Müller 1928). The *net* charge density can be calculated from a knowledge of the  $\zeta$ -potential and the concentration and type of the electrolyte.

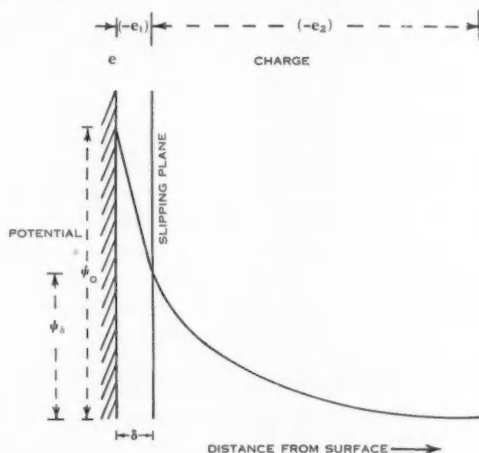


Fig. 1.—Graphical representation of the variation of charge and potential with distance from a solid-solution interface.

(ii) An equation due to Bull and Gortner (1931) requiring a knowledge of both  $\zeta$ -potential and surface conductance. A similar treatment has been presented by Abramson (1932).

Investigation showed that the second method was essentially unsound, and an alternative treatment was therefore developed. The resulting equation was applied to some surface conductance results on oxide minerals in water.

## II. CALCULATION OF CHARGE DENSITIES FROM $\zeta$ -POTENTIALS (METHOD 1)

Following Verwey and Overbeek (1948), the charges and potentials in the electrical double layer at a solid-solution interface may be represented as in Figure 1.

$\delta$  is the distance from the solid surface at which movement of liquid begins in electrokinetic experiments, that is, the slipping plane.  $e_1$  is the charge in



the compact part of the double layer, whilst  $e_s$  is the charge in the diffuse layer. It is reasonable to assume that the  $\zeta$ -potential corresponds to the potentials  $\psi_s$  at the inner limit of the diffuse layer, in which case the net charge density (charge per unit area) of the diffuse layer is given by the equation

$$\rho' = \pm \sqrt{\left(\frac{DRTe}{2\pi \times 1000}\right)} \sqrt{\left[\frac{1}{z_c} (e^{-z_c \epsilon \zeta / kT} - 1) + \frac{1}{z_a} (e^{z_a \epsilon \zeta / kT} - 1)\right]}, \quad \dots (2)$$

where  $e$  = electrolyte concentration (mol/l),

$z_c$  and  $z_a$  = valency of cations and anions respectively,

$\epsilon$  = electronic charge.

For the case in which  $z_c = z_a$ , (2) reduces to

$$\rho' = \pm \left(\frac{DRTe}{1000\pi}\right) \sinh \frac{z\epsilon\zeta}{kT}, \quad \dots \dots \dots (3)$$

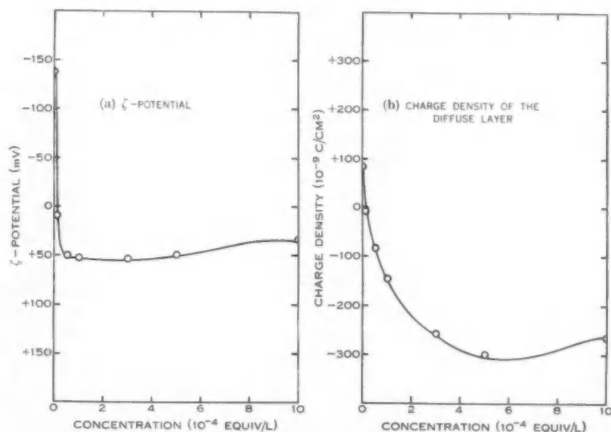


Fig. 2.—Variation of (a) the  $\zeta$ -potential and (b) the net charge density of the diffuse layer of cassiterite ( $\text{SnO}_2$ ) with the concentration of hydrochloric acid. The  $\zeta$ -potential has been given the sign of the solid surface, whilst the charge density has the sign of the diffuse layer.

The derivation of these equations assumes a Boltzmann distribution of ions in the diffuse layer. The value of  $\zeta$  to be inserted in (2) or (3) may be in error because of uncertain values of  $\eta$  and  $D$  in (1). The strong electric field in the diffuse layer is believed to cause a decrease of the dielectric constant (Grahame 1950; Booth 1951*a*, 1951*b*; Conway, Bockris, and Ammar 1951), whilst electroviscous effects increase the viscosity of the liquid in the diffuse layer (Elton 1948). In consequence the values of  $\eta$  and  $D$  will depend on the properties of the double layer, and will vary with distance from the surface. Insertion of

bulk values of these quantities in (1) will thus not lead to absolute values of  $\zeta$ -potential.

Comparisons between  $\zeta$  and  $\rho'$  for the influence of hydrochloric acid, sodium hydroxide, and potassium hydroxide on the electrical double layer of a negatively charged sample of the mineral cassiterite ( $\text{SnO}_2$ ) are shown in Figures 2 and 3 (data from O'Connor and Buchanan 1953). As is to be expected from (2) and (3), the curves of  $\zeta$ -potential *versus* concentration and charge density *versus* concentration are of generally similar form, thus providing justification for the qualitative discussion of  $\zeta$ -potential curves in terms of charge density curves (Buchanan and Heymann 1948*a*, 1948*b*, 1949; O'Connor and Buchanan 1953).

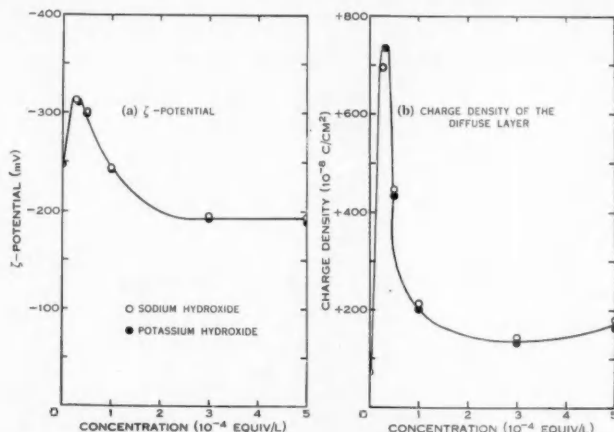


Fig. 3.—Variation of (a) the  $\zeta$ -potential and (b) the net charge density of the diffuse layer of cassiterite ( $\text{SnO}_2$ ) with the concentration of sodium hydroxide and potassium hydroxide. The  $\zeta$ -potential has been given the sign of the solid surface, whilst the charge density has the sign of the diffuse layer.

It should be emphasized that  $\rho'$  calculated from (2) is the *net* density of the diffuse layer. When ions of both signs are present in the layer, as is usually the case when electrolytes are added to the system,  $\rho'$  will differ from the *total* ion concentration.

### III. CALCULATION OF CHARGE DENSITIES FROM SURFACE CONDUCTANCES

A simplified derivation of the Bull and Gortner (1931) equation, retaining the essential features of the original method, is presented below.

The current  $I_s$  carried in the surface layer on the application of a potential  $V$  to a capillary or porous plug is given by the product of the velocity  $u$ , the charge per unit area  $\rho$ , and the perimeter of the cross section  $S$ , that is,

$$I_s = u \cdot \rho \cdot S. \quad (4)$$

The electric force acting on unit area is  $\rho(dV/dx)$ , whilst the viscous force per unit area retarding flow is  $\eta(u/d)$ , where  $\eta$  is the coefficient of viscosity of the

liquid, and  $d$  the distance of the layer from the plane at which  $u$  is equal to zero. When flow takes place at a constant rate

$$\eta \frac{u}{d} = \rho \frac{dV}{dx},$$

or

$$u = \frac{\rho d}{\eta} \frac{dV}{dx}. \quad (5)$$

Substituting for  $u$  in (4), we have

$$I_s = \frac{\rho^2 d}{\eta} \cdot S \cdot \frac{dV}{dx}. \quad (6)$$

An analogous expression can be written for surface current, as the product of the surface conductance, the perimeter of the capillary, and the potential gradient, namely,

$$I_s = K'_s \cdot S \cdot \frac{dV}{dx}, \quad (7)$$

in which

$$K'_s = K_s \cdot \frac{A}{S}, \quad (8)$$

$K'_s$  is the surface conductance ( $\Omega^{-1}$ ) defined by Bikerman (1933, 1935, 1940), whilst  $K_s$  is the measured surface conductance ( $\Omega^{-1} \text{ cm}^{-1}$ ), obtained as the difference between the specific conductance of the plug, or capillary filled with liquid  $K'$ , and the bulk conductance of the liquid  $K$ , and  $A$  is the area of cross section of the capillary.

From (6) and (7) it follows that

$$K'_s = \frac{\rho^2 d}{\eta}, \quad (9)$$

and that

$$K_s = \frac{\rho^2 d}{\eta} \cdot \frac{S}{A}. \quad (10)$$

Furthermore, if we make the usual simplifying assumption that the diffuse layer can be regarded as a parallel plate condenser, that is,

$$d = \frac{\zeta D}{4\pi\rho},$$

we may write

$$\rho = \frac{4\pi K_s \eta}{\zeta D} \cdot \frac{A}{S}, \quad (11)$$

and

$$d = \left( \frac{\zeta D}{4\pi} \right)^2 \cdot \frac{S}{\eta K_s A}. \quad (12)$$

Equation (11) gives values of  $\rho$  independent of  $\eta$  and  $D$  since these quantities cancel on substituting  $\zeta$  from equation (1) in equation (11). However,  $d$  derived from equation (12) will remain dependent on  $\eta$ .

The use of equation (11) should be confined to those cases in which the total and net densities of ions in the diffuse layer are identical. This is because instances may occur in which, with approximately equal numbers of positive and negative ions in the diffuse layer, the  $\zeta$ -potential (and hence the net charge density) is very small, and yet the surface conductance, since it is determined by all the ions in the diffuse layer, will still be of appreciable magnitude. As pointed out in previous papers on the electrokinetics of inorganic solids (Buchanan and Heymann 1948*a*, 1948*b*, 1949; O'Connor and Buchanan 1953), this condition can arise as a result of preferential ion adsorption by the solid, the counterions remaining in the diffuse layer, and often being of opposite sign to those present initially. Under these conditions (11) would give a very large value for  $\rho$ . We conclude therefore that the above derivation is incorrect, the error occurring in the substitution for  $u$  in equation (4) of a general expression for electro-osmotic flow (equation (5)), the former quantity being the rate of movement of ions in the surface layer, and the latter, the rate of movement of liquid as a result of momentum imparted to it by the moving ions. This difference between the rate of movement of ions in the diffuse layer and the liquid in that layer has been recognized previously in a discussion of surface conductance by Cole (1933).

An alternative treatment avoiding the difficulties of the Bull and Gortner derivation is presented in the following discussion. The measured surface conductance of a capillary (or series of capillaries) filled with liquid is a specific conductance, since it is the difference between the specific conductance of the liquid contained in the capillary  $K'$  and the bulk specific conductance of the liquid  $K$ . Although due to the excess of ions near the surface, it may be regarded for the present purpose as an additional conductance in each unit cube of the liquid in the capillary. If  $n$  is the number of ions apparently in excess in each cube, then the number in excess in the "cross section" (1 cm deep) will be  $A \times n$ , where  $A$  is the area of cross section. Since these ions are distributed over the walls of the capillary, the number associated with 1 cm<sup>2</sup> of surface is  $A \times n/S$ , where  $S$  is the circumference of the capillary, that is

$$\rho = A \cdot \frac{n}{S}, \quad \dots \dots \dots (13)$$

in which  $\rho$  is the charge density in ions/cm<sup>2</sup>. The ratio  $A/S$  can be calculated for a porous plug (set of tortuous capillaries), as shown in Section IV (a). To evaluate  $n$ , we write

$$l = 1000 \frac{K_s}{c},$$

or

$$c = 1000 \frac{K_s}{l}, \quad \dots \dots \dots (14)$$

assuming for simplicity that only one kind of ion contributes to the surface conductance;  $l$  is the *equivalent* ionic conductance of the ion concerned, and  $c$  is the concentration in g-equiv/l of this ion. Hence we may write for  $n$

$$n = \frac{cN}{1000},$$

and therefore

$$n = \frac{1000K_s}{l} \cdot \frac{N}{1000} = \frac{K_s N}{l}, \quad \dots\dots\dots (15)$$

where  $N$  is Avogadro's number. On substituting for  $n$  in (13), we have

$$\rho = \frac{A}{S} \cdot \frac{K_s N}{l}, \quad \dots\dots\dots (16)$$

Provided the conditions assumed in the derivation are complied with, equation (16) enables the charge density to be calculated from one electrokinetic quantity, namely, surface conductance. It has the further advantage of taking account of the mobility of the particular ionic species contributing to this conductance. On the other hand, some uncertainty is introduced since it is not known by how much the mobility of ions in the surface layer differs from that in the bulk solution; they may be retarded by the field of force of the surface and accelerated by electroosmotic effects. In the discussion in Section V relating to mineral oxides in water, it is assumed that the electrical double layer arises by ionization of surface hydroxyl groups, and hence it is probable that the diffuse layer makes the main contribution to surface conductance. In such cases, no large error should be introduced by using normal ionic mobilities. Equation (16) cannot be used in its present form when the diffuse layer consists of ions of more than one species unless they have equal mobilities, since, in general, the concentration of each species and, therefore, the contribution to the total surface conductance will not be known.

#### IV. DETERMINATIONS FOR POROUS PLUG PACKINGS

##### (a) Calculation of the Ratio $A/S$

For flow through a porous bed it has been shown by Carman (1948) and Wyllie and Spangler (1952) that

$$u = \frac{\varphi m^2 P}{k_0 \eta L} \left( \frac{L}{L_c} \right)^2, \quad \dots\dots\dots (17)$$

where  $u$  = velocity of flow (cm sec<sup>-1</sup>),\*

$\varphi$  = porosity of the plug,

$\eta$  = coefficient of viscosity (poises),

$k_0$  = shape factor,

$P$  = pressure forcing liquid through the plug (dyn cm<sup>-2</sup>),

$\left( \frac{L}{L_c} \right)^2$  = tortuosity  $T$ ,  $L$  being the length of the plug and  $L_c$  the average path length, and

$m = \frac{A}{S}$  (hydraulic radius).

\*  $u$  is the velocity of flow calculated assuming the volume flowing occupies the total area  $\pi R^2$ .

For a plug of length  $L$  cm, radius  $R$  cm, and with fluid flowing at a rate of  $Q$  c.c. min<sup>-1</sup> cm<sup>-1</sup> Hg, then

$$u = \frac{QP}{60 \times 13.6 \times 980 \times \pi R^2}, \quad \dots \quad (18)$$

and

$$m = \frac{A}{S} = \left( \frac{\eta L k_0 T Q}{\pi R^2 \varphi 8 \times 10^5} \right)^{\frac{1}{2}}, \quad \dots \quad (19)$$

The tortuosity  $T$  is calculated in the following manner. We may write for the cell constant of the porous plug

$$C = \frac{L_e}{A}, \quad \dots \quad (20)$$

where  $L_e$  is the effective path length between the electrodes at either end of the plug, and  $A$  is the effective area for ionic migration. Following the treatment of Slawinski (1926) we have

$$\frac{A}{\pi R^2} = \frac{L}{L_e} \varphi, \quad \dots \quad (21)$$

and hence

$$T = \left( \frac{L_e}{L} \right)^2 = \frac{C \pi R^2 \varphi}{L}. \quad \dots \quad (22)$$

Substituting for  $T$  in (19), we obtain

$$\frac{A}{S} = \left( \frac{\eta k_0 Q C}{8 \times 10^5} \right)^{\frac{1}{2}}. \quad \dots \quad (23)$$

Wyllie and Spangler (1952) concluded, after experimental investigations and a survey of published data, that the factor  $k_0$  has a value close to 2.7 and hence

$$\frac{A}{S} = 0.00184 (C \eta Q)^{\frac{1}{2}}. \quad \dots \quad (24)$$

#### (b) The Tortuosity

Following Buchanan and Heymann (1948a) we may write for the cell constant of a porous plug

$$C = \frac{L}{a \varphi \sigma}, \quad \dots \quad (25)$$

where  $\sigma$  is the "shape factor". As shown in Section IV (a), we may also write

$$C = \frac{LT}{a \varphi}, \quad \dots \quad (22)$$

where  $a = \pi R^2$ . Consequently

$$\sigma = \frac{1}{T} = \left( \frac{L}{L_e} \right)^2. \quad \dots \quad (26)$$

The factor  $\sigma$  is thus the square of the ratio of the length of the plug to the mean path length for ionic migration through the plug.

## V. RESULTS FOR MINERAL OXIDES

Surface charge densities for five naturally occurring oxides in water have been calculated using (2) and (16). The water was doubly distilled, the second time from alkaline  $\text{KMnO}_4$ , and was considered to be free of electrolyte impurities other than  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions. It was taken to contain  $1 \times 10^{-6}$  g-ions of  $\text{H}^+$  ion/l, and this value for  $c$  was used in (2). All the oxides possessed negative surfaces, and the diffuse layer was therefore assumed to consist of  $\text{H}^+$  ions (O'Connor and Buchanan 1953). The method of determining  $K_s$  (Table 1, column 6) has been described previously by O'Connor and Buchanan (1953). It is the difference in specific conductance of the water contained in a porous plug of the solid and the bulk specific conductance of the same water measured outside the porous plug.  $K_s$  therefore contains any contribution which the electrical double layer might make to the conductance of the system. The porous plugs in each case consisted of the minerals ground to  $-22+72$  mesh, and were packed in a streaming potential cell between perforated platinum electrodes.

Several of the oxides, for example, haematite ( $\text{Fe}_2\text{O}_3$ ), cassiterite ( $\text{SnO}_2$ ), and rutile ( $\text{TiO}_2$ ), exhibited appreciable measured "surface conductances" determined as the difference in conductance of liquid in the porous plug and in bulk. As the subsequent discussion will show, these effects are probably mainly due to the semiconducting properties of the particular oxides, and it is likely that the true surface conductances are comparatively small.

In Table 1, column 7 records the charge densities (in e.s.u.  $\text{cm}^{-2}$ ) calculated from  $\zeta$ -potentials using equation (2), whilst column 9 gives the values calculated from measured surface conductances (column 6). For these systems  $\rho'$  and  $\rho$  should be comparable since the diffuse layer probably consists of one ionic species only, namely  $\text{H}^+$  ions. In view of the uncertainties attached to the use of either equation (2) or equation (16), and also in view of the assumption in the latter equation of a constant and normal ionic mobility in the diffuse layer, which implies a different model in the two cases, it is thought that a factor of 2 or 3 would constitute reasonable agreement. This is the case only for corundum ( $\text{Al}_2\text{O}_3$ ) and quartz ( $\text{SiO}_2$ ), whilst for  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and to a lesser extent for  $\text{TiO}_2$ , the charge densities calculated from surface conductances are much greater than those calculated from  $\zeta$ -potentials. This observation is emphasized by the ratio of measured to calculated surface conductance  $K_s/K_s^c$  (Table 1, column 11), the latter being derived from the  $\zeta$ -potential using equations (2) and (16), a procedure used in principle by Urban and White (1932), Urban, White, and Strassner (1935), and Bikerman (1933). It seems certain that the large value of this ratio for  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ , and  $\text{TiO}_2$  is to be attributed to the semiconducting properties of these oxides, since each is known to be a metal excess conductor. Alternatively, for  $\text{Fe}_2\text{O}_3$  magnetite impurity could be responsible for the effects.  $\text{Al}_2\text{O}_3$ , on the other hand, exhibits conductivity only at elevated temperatures, and  $\text{SiO}_2$  not at all.

It is worth noting that the surface conductances to be expected  $K_s^c$  in the macrocrystalline systems investigated (crystals  $> 200$  mesh) are all of the order of  $10^{-7}$  to  $10^{-8} \Omega^{-1} \text{cm}^{-1}$  (Table 1, column 10). These values are in fact little

TABLE I  
CHARACTERISTICS OF MINERAL OXIDE PLUG PACKINGS

I	2	3	4	5	6	7	8	9	10	11
Mineral	$\zeta^*$ (mV)	Cell Constant $C$ (cm <sup>-1</sup> )	Shape Factor $\sigma$	$\frac{S}{A}$ (calc. from (24)) (cm <sup>-1</sup> )	$K_s$ ( $\times 10^{-10}$ cm <sup>-1</sup> )	$\rho'$ (calc. from (2)) (e.s.u. cm <sup>-2</sup> )		$\rho$ (calc. from (16)) (e.s.u. cm <sup>-2</sup> )	$K_s$ (calc. from $\rho'$ using (16)) ( $\times 10^{-10}$ cm <sup>-1</sup> )	$\frac{K_s}{K_s^c}$
Quartz (SiO <sub>2</sub> )	..	19.8	0.48	1383	0.22	157	32.7	147	0.23	0.96
Corundum (Al <sub>2</sub> O <sub>3</sub> )	..	7.78	0.53	1118	0.04	22.4	4.66	29	0.027	1.48
Rutile (TiO <sub>2</sub> )	..	5.38	0.52	1659	0.17	24.2	5.04	89	0.043	3.95
Cassiterite (SnO <sub>2</sub> )	..	19.5	0.45	570	5.70	261	54.3	8620	0.16	35.6
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	..	26.3	0.63	729	23.7	36.2	7.54	27.010	0.029	816

\* Sign refers to solid.



greater than the probable errors of measurement, since the water has a conductivity of about  $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  and is subject to small uncontrollable variations.

It is evident from the above discussion that (16) should only be applied to those systems in which the solid makes no contribution to the conductance of the system. Essentially similar conclusions on surface conductance measurements have been reached by Overbeek (1952) from a survey of published data on glass. Measured values were often greatly in excess of those calculated from  $\zeta$ -potentials, and Overbeek suggested that a swollen surface layer on the glass was providing the additional conductance.

In view of this conclusion and of the results presented in the present paper, it seems likely that little significance should be attached to surface conductance measurements, unless they are concerned with solids having very large surface areas. Clays are probably suitable in this respect, and an experimental study of kaolin is at present being carried out in order to test this hypothesis.

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## REDUCTION BY DISSOLVING METALS

### X. AROMATIC COMPOUNDS CONTAINING ELECTRON SINKS

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[Manuscript received February 22, 1954]

#### Summary

The general features are reviewed of the reduction by dissolving metals of aromatic compounds carrying electron-attracting groups. The reductions by sodium-ammonia solutions of 2-methylamino-, 3-methoxy-, 3,4-dimethoxy-, and 3,4,5-trimethoxybenzoic acid, of 3-ethoxyphenylbut-2-ene, and of 2-phenylimidazoline have been investigated.

#### I. COURSE OF REDUCTION OF BENZOIC ACIDS

The formulae below summarize briefly the postulated stages in the reduction of sodium benzoate to the salt of hexahydrobenzoic acid (II) by means of sodium and alcohols. The expected primary product is the 1,4-dihydro-derivative (e.g. I) (Birch 1950*a*, 1950*b*) and it is significant that 4-hydroxybenzoic acids cannot be reduced (Baudisch, Hibbert, and Perkin 1909); in alkaline solution the 4-hydroxyl group will be present as phenoxide ion, thus tending to prevent the formation of an anionic 4-carbon atom. The 2- and 4-alkoxybenzoic acids lose the alkoxy-group, presumably by transference of a negative charge from carbon to oxygen. 2-Hydroxybenzoic acids give rise to pimelic acids by ring-opening of the intermediate *cyclohexanonecarboxylic acid* (i.e. the tetrahydro-derivative). The effect of alkyl groups is to make the reductions of the ring more difficult, as would be expected from their electron-repelling character. Practical applications of classical dissolving metal reductions are often limited by the varying degrees of hydrogenation encountered in mixed products and by the occurrence of fission reactions. Moreover, at high temperatures the reversible formation of aldehydes from alkyl oxides tends to introduce alkyl groups into phenol and amino acids (e.g. Bauer and Einhorn 1901). The present work was undertaken to explore the theoretical aspects of reduction by the sodium-ethanol-liquid ammonia reagent and its practical applications to the reductions of compounds containing electron sinks. This reduction process often has the advantage over classical dissolving metal and catalytic hydrogenation methods that it permits partial hydrogenation in good yield and with high structure-specificity. So far it has been used almost solely with compounds containing only electron-repelling groups attached to benzene rings.

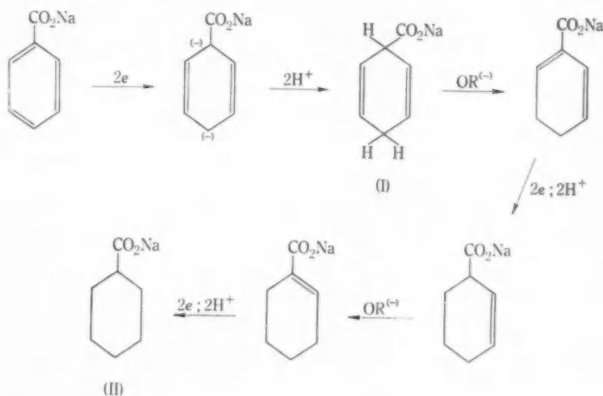
The protection of the electron-attracting carbonyl group has also been investigated in order to regenerate it after reducing a benzene ring. However,

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only with acids are the characteristic orientation properties of electron sinks preserved since other electron sinks are themselves reduced before the benzene ring, or if protected necessarily lose their electron-attracting nature.

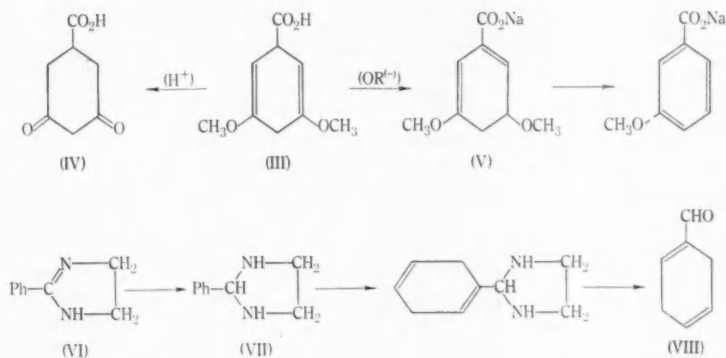
## II. REDUCTION OF SOME BENZOIC ACID DERIVATIVES IN LIQUID AMMONIA

2-Methylbenzoic acid has already been reduced with sodium and ethanol in liquid ammonia to 1,4-dihydro-2-methylbenzoic acid (Birch 1950a). The reduction of 3-methoxybenzoic acid has now been shown to result somewhat surprisingly in a 3-methoxytetrahydrobenzoic acid, since acid hydrolysis gives the known 3-carboxycyclohexanone. Conjugation of the double bonds in the initial dihydro-derivative must therefore occur very readily in this case. The same product is obtained from veratric acid (3,4-dimethoxybenzoic acid) with the expected removal of the 4-methoxyl group.



Removal of methoxyl also occurs from 3,4,5-trimethoxybenzoic acid to form 1,4-dihydro-3,5-dimethoxybenzoic acid (III) because acid hydrolysis of the product produces 3,5-diketocyclohexanecarboxylic acid. The lack of further reduction must be due to the greater difficulty of conjugation of the double bonds; the process would involve the movement of a double bond from a position of hyperconjugation with a methoxyl group. Conjugation can be accomplished by refluxing with sodium butoxide in butanol when 3-methoxybenzoic acid results in high yield by loss of methanol from the initial conjugated diene (V). Semmler (1908) has already noted the formation of 3-methoxybenzoic acid by reduction of 3,4,5-trimethoxybenzoic acid with sodium and ethanol, without proving any intermediate stages. Removal of the 4-methoxyl group is doubtless greatly facilitated by the carboxyl group, but 1,2,3-trimethoxybenzene itself loses the central methoxyl group, since reduction and hydrolysis give 1,3-diketocyclohexane (Birch 1947). Phloroglucinol trimethyl ether also loses a methoxyl group to give, finally, 1,3-diketocyclohexane.

The reduction of some 2-methoxybenzoic acid derivatives has already been examined (Birch, Murray, and Smith 1951) in an endeavour to prepare *cyclohexenones* having a double bond in a different position from that found in the product of reduction and hydrolysis of the methoxybenzenes themselves. The preponderant removal by hydrogenolysis of the methoxyl group, and therefore, the low eventual yield of ketone makes the reaction of no preparative interest. The reduction of 2-methylaminobenzoic acid has now been examined on the theory, based on a comparison of the acid pK's of ammonia and methanol (c. 34 and 18 respectively), that removal of  $(-)\text{NHCH}_3$  will be more difficult than that of  $(-)\text{OCH}_3$ . This expectation was substantiated, but only *cyclohexanone* was isolated after acid hydrolysis, and the method was not further investigated.



### III. PROTECTION OF CARBONYL GROUPS

Protection of a carbonyl group can be achieved by forming its enolate (Birch 1950b). This method is useful when experimental conditions are such that the enol is the strongest "acid" present. However, the presence of any "acids" such as an alcohol of comparable strength permits reduction of the group to occur (e.g. Pinder and Smith 1954). Conversion of a carbonyl group to a non-reducible group is readily achieved through formation of an acetal or an enol-ether, provided the double bond of the latter is not in a benzyl ether position. 3-Ketophenylbutane was converted to its enol ethyl ether, the benzene ring reduced, and 2',5'-dihydrophenyl-3-ketobutane formed by the action of acid. 1',1'-Diethoxymethylbenzene by the same process gave only hydrocarbon material (see also Pinder and Smith 1954).

In order to extend protection to aromatic aldehydes and ketones lacking a 4-methoxyl group (cf. Birch, Quartey, and Smith 1952) the device was tried of replacing the oxygen of an acetal by nitrogen. As already noted, hydrogenolysis of such a structure would necessitate fission of a carbon-nitrogen bond with the formation of an anionic nitrogen fragment. 2-Phenylimidazoline (VI) was reduced with two equivalents of sodium to give 2-phenylimidazolidine (VII) hydrolysed by acid to benzaldehyde. This process or a modification might be

useful for converting nitriles into aldehydes. Further reduction of the imidazolidine followed by acid hydrolysis gave a dihydrobenzaldehyde (VIII) as a sharp-smelling, rather unstable oil, oxime, m.p. 97–98 °C semicarbazone, m.p. 207–208 °C. This should be 2,5-dihydrobenzaldehyde, since the substituent on the benzene ring should behave in the reduction as a simple electron-repelling group. The oxime differs from that of the known 2,3-dihydrobenzaldehyde oxime, m.p. 39 °C (Langenbeck *et al.* 1942).

#### IV. EXPERIMENTAL

(a) *Reduction of 3-Methoxybenzoic Acid and Veratric Acid.*—3-Methoxybenzoic acid (5 g) in ethanol (15 c.c.) and liquid ammonia (150 c.c.) was reduced by the slow addition with stirring of sodium (3 g). After reaction was complete, ammonium chloride (25 g) in water (60 c.c.) was added and the ammonia evaporated. The solution was acidified with hydrochloric acid, boiled for about 1 min, cooled, and thoroughly extracted with ether. Removal of the solvent gave an oil, b.p. 142–145 °C/2.5 mm, which solidified and was recrystallized from a mixture of benzene and light petroleum (b.p. 40–60 °C) as colourless needles (3.3 g), m.p. 76 °C, semicarbazone, m.p. 183–184 °C, 2,4-dinitrophenylhydrazone, m.p. 230 °C. *cyclohexanone-3-carboxylic acid* has m.p. 76 °C, semicarbazone, m.p. 184 °C (Dobson, Ferns, and Perkin 1909). The ultraviolet absorption curve showed the expected low intensity maximum at 278 m $\mu$ . Veratric acid similarly reduced gave rise to the same product, m.p. 76 °C.

(b) *Reduction of 3,4,5-Trimethoxybenzoic Acid.*—The acid (10.6 g) in ethanol (75 c.c.) and ammonia (500 c.c.) was reduced with sodium (6 g). After completion of the reaction ammonium chloride (25 g) was added and most of the ammonia evaporated. Hydrochloric acid (2N; 100 c.c.) was then added and the solution boiled for a few minutes. After cooling the solution was thoroughly extracted with ether. The 3,5-diketocyclohexanecarboxylic acid solidified and was crystallized from ethyl acetate as colourless needles (5 g), m.p. 180 °C (Found: C, 53.9; H, 5.1%. Calc. for  $C_8H_8O_4$ : C, 53.8; H, 5.1%). It condensed with formaldehyde to a derivative, m.p. 270 °C.

(c) *Conversion of 3,4,5-Trimethoxybenzoic Acid to 3-Methoxybenzoic Acid.*—After reduction of 3,4,5-trimethoxybenzoic acid (10.6 g) as above, to the ammonia solution was added a solution of sodium (10 g) in butanol (100 c.c.), and the mixture refluxed so as to allow the ammonia to escape. After 2 hr, ether (200 c.c.) was added and the mixture extracted with water. Acidification of the aqueous solution gave 3-methoxybenzoic acid (5.3 g), m.p. 105 °C undepressed by an authentic specimen.

(d) *Reduction of N-Methylantranilic Acid.*—N-Methylantranilic acid (15.1 g) in a mixture of ethanol (500 c.c.), ether (100 c.c.), and ammonia (300 c.c.) was reduced with sodium (10 g). After acid hydrolysis and ether extraction in the usual manner an oil was obtained (c. 25% yield) giving rise to *cyclohexanone-2,4-dinitrophenylhydrazone*, m.p. 156 °C undepressed by an authentic specimen. The ultraviolet absorption curve of the ketone showed only a low intensity maximum at 263 m $\mu$ , proving the absence of *cyclohex-2-enone*.

(e) *Reduction of 1,3,5-Trimethoxybenzene.*—1,3,5-Trimethoxybenzene (4.2 g) in ethanol (20 c.c.) and ammonia (150 c.c.) was reduced with sodium (2 g) and the product worked up by hydrolysis and ether extraction in the usual manner. The *cyclohexan-1,3-dione* formed colourless prisms, m.p. 105 °C, oxime, m.p. 155 °C, formaldehyde derivative, m.p. 133 °C; the authentic compounds have m.p. 105–106 °C, m.p. 154–157 °C, and m.p. 132–133 °C respectively (Merling 1894).

(f) *2',5'-Dihydrophenylbutan-3-one.*—Phenylbutan-3-one (15 g) and ethyl orthoformate (15 g) were mixed and a few drops of an absolute ethanolic solution of hydrogen chloride added. There was an immediate evolution of heat and after leaving for 8 hr the mixture was distilled and 3-ethoxyphenylbutene collected, b.p. 142–146 °C/20 mm (14 g) (Found: C, 81.1; H, 9.2%. Calc. for  $C_{12}H_{14}O$ : C, 81.8; H, 9.1%). The ethoxyphenylbutene (24 g) in ethanol (50 c.c.) and ammonia (800 c.c.) was reduced with sodium (18 g) and the product worked up by dilution

with water and ether extraction. It was a colourless oil, b.p. 190–194 °C/37 mm. It was refluxed with hydrochloric acid (3%) for 30 min and the 2',5'-dihydrophenylbutan-3-one formed was purified through the bisulphite compound, b.p. 122–130 °C/18 mm (13.5 g) (Found: C, 80.0; H, 9.1%. Calc. for  $C_{10}H_{14}O$ : C, 80.0; H, 9.3%). The semicarbazone formed colourless prisms, m.p. 148 °C depressed to about 138 °C by the derivative of phenylbutan-3-one, m.p. 142 °C (Found: C, 63.8; H, 8.0%. Calc. for  $C_{11}H_{17}ON_3$ : C, 63.8; H, 8.2%).

(g) *Reduction of 2-Phenylimidazoline*.—(i) 2-Phenylimidazoline (7.3 g) (Oxley and Short 1947) in ethanol (20 c.c.) and ammonia (100 c.c.) was reduced by the addition of sodium (2.3 g). Water (100 c.c.) was added, and after leaving overnight colourless needles, m.p. 53–54 °C, had separated. Owing to its instability this substance could not be satisfactorily purified for analysis. The substance was dissolved in hydrochloric acid (2N; 25 c.c.) an oil separating, b.p. 176–178 °C, semicarbazone, m.p. 221 °C, 2,4-dinitrophenylhydrazone, m.p. 232–234 °C, undepressed by authentic derivatives of benzaldehyde. Oxidation gave benzoic acid, m.p. 121 °C. Conversion of the oil to the semicarbazone gave 6.12 g (75% overall yield).

(ii) 2-Phenylimidazoline (14.6 g) in ethanol (50 c.c.) and ammonia (300 c.c.) was reduced with sodium (20 g). Water (200 c.c.) was added and the product extracted with ether (500 c.c.). On removal of the ether a yellow oil (10.3 g) remained. This was dissolved in hydrochloric acid (N), and after 1 hr the solution was extracted with ether and the extract distilled with addition of methylene blue giving 2,5-dihydrobenzaldehyde as pale yellow, sharp-smelling oil, b.p. 90–95 °C/25 mm (Found: C, 78.2; H, 7.8%. Calc. for  $C_7H_8O$ : C, 77.8; H, 7.4%). It was unstable and was rapidly oxidized by air to benzoic acid. The oxime crystallized as colourless needles from light petroleum (b.p. 60–90 °C), m.p. 97–98 °C (Found: C, 69.0; H, 7.5%. Calc. for  $C_7H_9ON$ : C, 68.3; H, 7.3%). The semicarbazone crystallized from ethanol as cream coloured prisms, m.p. 207–208 °C (Found: C, 58.6; H, 6.8%. Calc. for  $C_8H_{11}ON_3$ : C, 58.2; H, 6.7%). A repetition of the reduction on 2-phenylimidazoline (7.3 g) gave finally, the semicarbazone (4.40 g) representing 53% overall yield of 2,5-dihydrobenzaldehyde.

## V. ACKNOWLEDGMENTS

The authors are indebted to Professor S. M. Mukherji who carried out the reduction of 3-ethoxyphenylbutene. One of us (S.S.) is indebted to the University of Sydney for the award of an I.C.I. Fellowship.

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## REDUCTION BY DISSOLVING METALS

### XI. THE ACTION OF POTASSIUM AND ALCOHOLS ON SOME MONOBENZENOID SUBSTANCES

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[Manuscript received February 22, 1954]

#### Summary

An investigation has been made of some of the effects of structure and of conditions on the extent of reduction by potassium and alcohols of a number of monobenzenoid substances (see Table 1).

#### I. INTRODUCTION

It is well known (Birch 1950) that alkali metals and alcohols in liquid ammonia can reduce monobenzenoid compounds to  $\alpha\delta$ -dihydro-derivatives. It was briefly reported (Birch 1947) that potassium and alcohols can bring about the same reduction in anisole derivatives. A further study has now been carried out with the object of comparing the yields obtainable from benzenes variously substituted with alkyl-, methoxy- and dimethylamino-groups in relation to possible reaction mechanisms. The process has the advantage for this purpose over the metal-alcohol-ammonia combinations that completely homogeneous solutions of the organic substances can be obtained. It has the disadvantage that the potassium forms a separate phase. However, all reductions were carried out as far as possible under the same conditions, and the results in any given case were usually reproducible within several per cent.

Estimation of the extent of reduction was carried out in two entirely different ways. The first method depends on the fact that the dihydroanisole and dihydroaniline derivatives on acid treatment give rise to ketones. These can then be quantitatively estimated as their 2,4-dinitrophenylhydrazones (method A or B). The second method, applicable to alkyl-dihydrobenzenes or dihydroanisoles, depends on the fact that they are quantitatively oxidized to the benzene or anisole by the action of lead tetra-acetate, and can accordingly be titrated using standard methods (method C). Usually these methods give results in good agreement, Table 1. They were checked against one another by using a sample of 2,5-dihydroanisole prepared by reduction with sodium and ethanol in liquid ammonia: method A 92.6 per cent.; method C 93.9, 93.7 per cent. This material, after standing for 5 days, gave the values: method A 83.4 per cent.; method C 83.8 per cent. It is well known that autoxidation to aromatic material occurs on leaving in air.

In Table 1 the amounts of different substances and alcohols employed are in molar ratios throughout, unless otherwise indicated, being based on the

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arbitrary choice of tolyl methyl ether (5.00 g), ethanol (40 ml), and potassium (3.2 g).

An attempted reduction of *m*-tolyl methyl ether with sodium and ethanol gave no product. A reduction of a mixture of *m*-tolyl methyl ether and toluene gave an estimate of total dihydrobenzenes (method *C*) 26.4, 27.0 per cent. and of dihydro-*m*-tolyl methyl ether (method *B*) 22.7 per cent. It is evident that the toluene has had little effect on the reduction of the *m*-tolyl methyl ether (27.3 per cent. alone, method *A*) in accord with the small extent of reduction of toluene alone (4.3 per cent., method *C*).

TABLE 1  
REDUCTION OF MONOBENZENOID COMPOUNDS

Compound	Alcohol	Reduction (%)		
		<i>A</i>	<i>B</i>	<i>C</i>
Anisole .. .. .	Ethanol	(i) 34.3 (ii) 34.8		36.8; 37.5
Anisole .. .. .	Butanol		42.5	42.5
<i>o</i> -Tolyl methyl ether ..	Ethanol	(i) 12.5 (ii) 8.6		13.7 9.1; 9.3
<i>m</i> -Tolyl methyl ether ..	Ethanol	27.3		
<i>m</i> -Tolyl methyl ether ..	Ethanol*	16.3		18.4
<i>m</i> -Tolyl methyl ether ..	Butanol		25.3	28.0
<i>m</i> -Tolyl methyl ether ..	<i>iso</i> Propanol		18.4	18.6
<i>m</i> -Tolyl methyl ether ..	Methanol		18.0	19.1
<i>p</i> -Tolyl methyl ether ..	Ethanol			35.6
<i>p</i> -Tolyl methyl ether ..	Butanol		(i) (ii) 36.1	34.8 38.2
Dimethylaniline .. ..	Ethanol		10.1	
Toluene .. .. .	Ethanol			4.3
2,6-Dimethylanisole ..	Ethanol	2.6		
2,4-Dimethylanisole ..	Ethanol	11.0		
3,5-Dimethylanisole ..	Ethanol	7.6		

\* 0.5 vol.

The conclusions which emerge from Table 1 are therefore: (i) The order of ease of reduction is anisole > *p*-tolyl methyl ether > *m*-tolyl methyl ether > *o*-tolyl methyl ether ≈ dimethylaniline > toluene. (ii) *n*-Butanol seems to be a slightly better reducing medium than ethanol; both are superior to *isopropanol* and methanol but differences in solvent effects are much less marked than those due to structure. (iii) The yields of reduction products from the monosubstituted benzenes are influenced by groups in the order  $\text{OCH}_3 > \text{N}(\text{CH}_3)_2 > \text{CH}_3$ , and an increase in the number of alkyl groups results in more difficult reduction.

In order to define further the solvent effects reduction of *m*-tolyl methyl ether was carried out in *isoamyl* alcohol at 85–95 °C (yield, method *A*, 21.6 per cent.) and at 130 °C (yield, method *A*, 18.3 per cent.). This result is incon-



clusive; it may be that the slightly lower yield at higher temperature is due to increasing side-reactions such as conjugation of the double bonds and further reduction.

Owing to an interruption in collaboration the effects of a number of alterations in structure have not yet been examined; discussion of the mechanism will therefore be postponed. It is worth noting, however, that the order of ease of reduction anisole > dimethylaniline > toluene is in the order of the inductive effects of the groups attached to the ring. The process may be of some practical importance for compounds insoluble in liquid ammonia.

## II. EXPERIMENTAL

(a) *Reduction Process.*—The potassium was purified by heating with pure dioxan, thus being obtained as clean metallic spheres which floated on the surface; the impurities sank to the bottom. The alcohols were purified by standard methods to obtain completely anhydrous material. The compound to be reduced (5.00 g of tolyl methyl ether or the mol. equiv. of other ethers) was dissolved in the alcohol (40.0 c.c. of ethanol or the mol. equiv. of other alcohols) in a flask (100 c.c.) fitted with a stirrer and reflux condenser. Potassium (3.2 g) was added in small pieces with vigorous stirring, the total time of addition being 45–60 min according to the rate of reaction; the temperature was kept at about 50–60 °C.

(b) *2,4-Dinitrophenylhydrazine Estimation.*—(i) *Method A.* After reduction, water (50 c.c.) was added and the solution extracted with ether (2 × 25 c.c.). The extract was added to a freshly prepared solution of 2,4-dinitrophenylhydrazine (4 g) in ethanolic sulphuric acid (5%; 400 c.c.). Ether was evaporated on the water-bath, ethanol added to make up the original volume, and the solution left for several days. The crystalline precipitate was then removed by filtration, washed with warm aqueous sulphuric acid (2N) and with hot water, dried at 110 °C, and weighed. In several cases (notably that of anisole) the cold ethanolic solution of the reagent was saturated with the 2,4-dinitrophenylhydrazone to avoid loss due to its slight solubility.

(ii) *Method B.* The ether extract (method A) was added to 2,4-dinitrophenylhydrazine (4 g) in hydrochloric acid (2N; 300 c.c.), the mixture shaken and then warmed. Finally the remaining ether and unreduced aromatic ether were removed by warming under reduced pressure, while hydrochloric acid (2N) was added to make up loss by evaporation. After leaving overnight the derivative was removed by filtration, washed with hot water (2 l.), dried, and weighed.

The derivative in each case was recrystallized and the m.p. agreed with that expected for the  $\alpha\beta$ -unsaturated ketone derivative (cf. Birch 1946) with the exception of that from 4-methylanisole which appeared to be a mixture of the derivatives from 4-methylcyclohex-2- and 3-enone. For anisole the unreduced material was shown to be unchanged by its b.p. and  $n_D$ ; acidification of the alkaline solution from the original reduction gave no phenol, so demethylation does not occur.

(c) *Lead Tetra-acetate Oxidation.*—(i) *Method C.* Lead tetra-acetate (Dimroth and Schweker 1923) was dissolved to a 0.1N solution in acetic acid purified by refluxing with chromium trioxide for 24 hr. To a weighed aliquot portion (c. 5%) of the ether extract from the reduction (see method A) an excess of lead tetra-acetate (0.1N; 10–25 c.c.) was added, and the solution shaken for a few minutes. To it was added 20 c.c. of a solution containing potassium iodide (20 g) and crystallized sodium acetate (500 g) in water (1 l.). The liberated iodine was titrated with thio-sulphate (0.1N) in the usual manner. A blank consisting of ether and the alcohol used in the reduction showed only a very small consumption of lead tetra-acetate.

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## LIQUID-VAPOUR EQUILIBRIA

### IV. THE SYSTEM ETHANOL+BENZENE AT 45 °C

By I. BROWN\* and F. SMITH\*

[Manuscript received March 31, 1954]

#### Summary

New liquid-vapour equilibrium data are given for the system ethanol+benzene at 45.00 °C. These data are used to calculate the excess free energy of mixing for this system.

#### I. INTRODUCTION

Liquid-vapour equilibrium data for this system have been measured at constant pressure by a number of workers, notably by : Tyrer (1912*a*, 1912*b*), Fritzweiler and Dietrich (1933), Uchida and Tezuka (1938), Ellis (1951, 1952), and Yerazunis (in press). Their measurements are not entirely in agreement. The only measurements at constant temperature, however, are those of Lehfeldt (1898) which we have shown to be thermodynamically inconsistent by the method of Herington (1947) and Redlich and Kister (1948). The present measurements were made to provide reliable isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of alcohol solutions.

#### II. EXPERIMENTAL

##### (a) Apparatus

The liquid-vapour equilibrium and vapour pressure measurements were made using the equilibrium still described by Brown (1952), pressure and temperature measurements were made by the methods of Brown and Ewald (1950), and the analysis by refractive index measurements using a Bellingham and Stanley Pulfrich type refractometer maintained at  $25.00 \pm 0.01$  °C.

##### (b) Purification and Properties of Components

The ethanol was purified by the method of Barker, Brown, and Smith (1953) and the benzene as described by Brown and Ewald (1951). The physical properties of the components are shown in Table 1.

##### (c) Analytical Method

The liquid and vapour samples were analysed by refractive index measurements. Eleven mixtures were made by weighing, allowing for the buoyancy of the air and the weight of air-vapour mixture of the first component displaced on adding the second. The refractive index-composition data are given in Table 2, where  $x_1$  is the mole fraction of ethanol in the mixture.

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In order to use the data in Table 2 for the analysis of liquid and condensed vapour samples a direct plot of refractive index against composition was impracticable. A graph against refractive index of the difference  $\Delta_0$  between the measured refractive index and the value calculated assuming a linear relationship

TABLE 1  
PHYSICAL PROPERTIES OF COMPONENTS

Property	Ethanol	Benzene
B.p./760 mm Hg (°C) .. ..	78.29	80.07
$d_4^{25.00}$ .. ..	0.78511	0.87359
$n_D^{25.00}$ .. ..	1.35929	1.49803
Vapour pressure 45.00 °C ..	172.87	223.74

with mole fraction also involved too many significant figures. A quadratic in  $n$  was taken out and values of the residual  $\Delta$  were calculated using equation (1)

$$\Delta = n - n_2 + x_1(n_2 - n_1) + 2.777(n - n_2)(n - n_1), \quad \dots \dots (1)$$

where  $n$ ,  $n_1$ , and  $n_2$  are the measured refractive indices of the mixture, pure ethanol, and pure benzene respectively. The calculated values of  $\Delta$  shown in Table 2 were plotted against  $n$ . The composition of the samples was then determined from (1) using the graph to determine values of  $\Delta$ .

TABLE 2  
REFRACTIVE INDEX-COMPOSITION DATA

$x_1$	$n_D^{25.00}$	$\Delta$
0.0000	1.49803	0.00000
0.0451	1.49401	+0.00072
0.0957	1.48885	+0.00080
0.1991	1.47790	+0.00087
0.2890	1.46776	+0.00070
0.3928	1.45533	+0.00041
0.4966	1.44219	+0.00017
0.5984	1.42815	-0.00021
0.6940	1.41392	-0.00058
0.8059	1.39555	-0.00099
0.9052	1.37772	-0.00088
0.9487	1.36923	-0.00073
1.0000	1.35929	0.00000

### III. LIQUID-VAPOUR EQUILIBRIUM DATA

The liquid-vapour equilibrium data are shown in Table 3 where  $x_1$  and  $y_1$  are the mole fractions of ethanol in the liquid and vapour respectively,  $P$  is the total pressure in standard mm Hg, and  $\alpha$  is the relative volatility given by  $\alpha = (y_1 x_2) / (y_2 x_1)$ .

TABLE 3  
ETHANOL+BENZENE AT 45.00 °C  
Experimental data and derived functions

$x_1$	$y_1$	$P$	$\alpha$	$\mu_1^E$	$\mu_2^E$	$G_x^E$
0.0374	0.1965	271.01	6.286	1335	5.4	55.1
0.0972	0.2895	296.53	3.782	1030	24.6	122.3
0.2183	0.3370	306.55	1.820	633.9	93.0	211.1
0.3141	0.3625	309.33	1.242	455.2	156.7	250.5
0.4150	0.3842	309.59	0.8791	315.9	236.2	269.3
0.5199	0.4065	307.46	0.6327	204.5	333.7	266.5
0.5284	0.4101	306.99	0.6205	198.8	340.3	265.5
0.6155	0.4343	302.05	0.4796	128.2	433.0	245.4
0.7087	0.4751	291.81	0.3720	74.0	540.2	209.8
0.8102	0.5456	271.08	0.2811	30.5	674.8	152.8
0.9193	0.7078	227.72	0.2127	6.2	829.5	72.6
0.9591	0.8201	203.28	0.1944	1.8	882.7	37.8

These data show that an azeotrope is formed at 45.00 °C having a mole fraction of ethanol of 0.375 and at a total pressure of 309.75 mm Hg.

#### IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials  $\mu_1^E$  and  $\mu_2^E$  and the excess free energy of mixing  $G_x^E$  were calculated from the equilibrium data using equations (2), (3), and (4). The values obtained (cal/g-mol) are given in Table 3.

$$\mu_1^E = RT \ln (Py_1/P_1^x) + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2, \quad \dots \quad (2)$$

$$\mu_2^E = RT \ln (Py_2/P_2^x) + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2, \quad \dots \quad (3)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \quad \dots \quad (4)$$

where  $P_1$  and  $P_2$  are the vapour pressures of the pure components,  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{12}$  are the second virial coefficients in the equations of state for the pure and mixed vapours,  $V_1$  and  $V_2$  are the liquid molar volumes.

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}, \quad T^\circ\text{K} = t^\circ\text{C} + 273.16.$$

The values of  $V_1$  and  $V_2$  were calculated from density data given by Timmermans (1950), the value of  $\beta_{11}$ (ethanol) was calculated by the method used by Barker, Brown, and Smith (1953), and that for benzene from the relation given by Allen, Everett, and Penney (1952), that is,

$$\beta_{22} = 0.070 - \frac{13.2 \times 10^4}{T^2} \quad \text{l/mole.}$$

To form an approximate estimate of  $\beta_{12}$  the following assumptions were made :

(i) That the second virial coefficient which ethanol would have if it did not form hydrogen bonds is given by the Berthelot equation,  $\beta'_{11} = B_1 - A_1/T^2$ .

(ii) That the mixed virial coefficient  $\beta_{12}$  is given by an equation of the Berthelot type,  $\beta_{12} = B_{12} - A_{12}/T^2$ .

(iii) That the values of  $B_{12}$  and  $A_{12}$  are given by the following combinations of the Berthelot constants for ethanol and benzene as determined from critical data.

$$B_{12} = \left( \frac{B_1^{\frac{1}{2}} + B_2^{\frac{1}{2}}}{2} \right)^3, \quad \left[ \frac{A}{B^2} \right]_{12} = \sqrt{\left[ \frac{A}{B^2} \right]_1 \times \left[ \frac{A}{B^2} \right]_2}.$$

Values of second virial coefficients and molar volumes at 45 °C (l.) used are :

$\beta_{11}$	$\beta_{22}$	$\beta_{12}$	$\delta_{12}$	$V_1$	$V_2$
-1.970	-1.236	-0.919	+1.367	0.060	0.092

The excess free energy data at 45.00 °C were fitted by the method of least squares to equation (5) :

$$G_x^E = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)^2 + d(x_1 - x_2)^3]. \quad \dots (5)$$

The values of the constants and the standard deviation  $\sigma$  of the fit were (in cal/g-mol) :

	$a$	$b$	$c$	$d$	$\sigma$
Two constant equation	+1092.4	-217.4	0	0	5.6
Three constant equation	+1072.7	-218.0	+162.0	0	2.3
Four constant equation	+1071.7	-170.6	+166.6	-136.3	0.9

Values of the second derivative of the total free energy of mixing with respect to  $x_1$  were also calculated and these gave no change of sign, showing that equation (5) with the above values of the constants does not indicate separation into two liquid phases.

The method of Herington (1947) and Redlich and Kister (1948) was used to test the thermodynamic consistency of the results which was shown to be satisfactory as the ratio of the areas above and below datum in a plot of  $(\mu_1^E - \mu_2^E)$  against  $x_1$  was 1.015.

The errors in  $G_x^E$  due to the errors in the measured quantities were estimated to be of the order of 3.5 cal/mole of which approximately half is due to errors in the refractometric analysis.

## V. CONCLUSIONS

Thermodynamically consistent values are given for the liquid-vapour equilibrium and excess free energy of mixing for the system ethanol + benzene at 45 °C. These data will be used to calculate the excess entropy of mixing for this system as soon as heat of mixing measurements have been completed. This system forms an azeotrope at 45.00 °C having a mole fraction of ethanol of 0.375 and a total pressure of 309.75 mm Hg.

## VI. ACKNOWLEDGMENTS

The authors thank Mr. W. Fock for his help in testing the data of Lehfeldt, Mr. O. H. Rigby for his help in the purification of the components, and Mr. J. A. Barker for his help with the preparation of the manuscript.

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## LIQUID-VAPOUR EQUILIBRIA

### V. THE SYSTEM CARBON TETRACHLORIDE + ACETONITRILE AT 45 °C

By I. BROWN\* and F. SMITH\*

[Manuscript received March 31, 1954]

#### Summary

Liquid-vapour equilibrium data are given for the system carbon tetrachloride + acetonitrile at 45.00 °C. These data are used to calculate the excess free energy of mixing for this system.

#### I. INTRODUCTION

The liquid-vapour equilibrium data for this system have not been recorded in the literature. The present measurements were made to provide isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of solutions of polar liquids.

#### II. EXPERIMENTAL

##### (a) Apparatus

The liquid-vapour equilibrium data and vapour pressure measurements were made by the methods used by Brown and Smith (1954). The analysis was by density measurements as used by Brown and Ewald (1950).

##### (b) Purification and Properties of Components

The carbon tetrachloride was purified by the method used by Barker, Brown, and Smith (1953). The acetonitrile was dried over anhydrous calcium chloride and carefully fractionated, using the column described by Brown and Ewald (1951), retaining fractions boiling over a range of 0.02 °C and having a constant density. The physical properties of the components are shown in Table 1.

TABLE I  
PHYSICAL PROPERTIES OF COMPONENTS

Property	Carbon Tetrachloride	Acetonitrile
B.p./760 mm Hg (°C)	76.65	81.57
$d_4^{25.00}$	1.58435	0.77656
$n_D^{25.00}$	1.45734	1.34154
$n_D^{20}$	1.4607	1.3443
Vapour pressure 45.00 °C	258.84	208.35

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The vapour pressure of acetonitrile was measured using the equilibrium still and the data are given in Table 2. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - B/(C + t),$$

where  $P$  is in standard mm Hg and  $t$  in  $^{\circ}\text{C}$ . The values of the constants found and the standard deviation  $\sigma$  of the fit are given in Table 2.

TABLE 2  
THE VAPOUR PRESSURE OF ACETONITRILE

$t$ ( $^{\circ}\text{C}$ )	$P$ (mm Hg)	Antoine Equation Constants
29.97	110.54	$A = 7.28034$ $B = 1420.20$ $C = 241.241$ $\sigma = 0.10$ mm Hg
37.42	152.71	
44.95	207.88	
45.01	208.47	
47.04	226.03	
47.06	226.16	
54.52	301.04	
67.28	475.37	
71.32	545.39	
81.54 <sub>6</sub>	759.39	
81.55 <sub>7</sub>	759.69	
81.56 <sub>4</sub>	759.83	

(c) Analytical Method

The liquid and vapour samples were analysed by density measurements; 11 mixtures were made by weighing. The density-composition data are given in Table 3, where  $x_1$  is the mole fraction of carbon tetrachloride in the mixture and  $n_D^{20}$  are refractive indices of the mixtures at  $20^{\circ}\text{C}$ .

TABLE 3  
DENSITY-COMPOSITION DATA

$x_1$	$d_4^{25.00}$	$\Delta$	$n_D^{20}$
0.0839	0.89338	+0.00258	1.3609
0.0933	0.90544	+0.00255	1.3627
0.1913	1.02234	+0.00093	1.3793
0.2857	1.12054	-0.00068	1.3933
0.4113	1.23264	-0.00155	1.4096
0.5088	1.30823	-0.00092	1.4204
0.6142	1.38045	+0.00039	1.4310
0.6972	1.43147	+0.00130	1.4385
0.8126	1.49523	+0.00191	1.4477
0.9174	1.54680	+0.00336	1.4550
0.9535	1.56343	+0.00047	1.4577



In order to use the data in Table 3 for analysis a method analogous to that used by Brown and Smith (1954) was employed. Values of the residuals  $\Delta$  in equation (1) were calculated from the density-composition data and graphed against density. The composition of samples was then calculated from the measured density using equation (1) and values of  $\Delta$  from the graph.

$$\Delta = d - d_2 + x_1(d_2 - d_1) + (d - d_1)(d - d_2)[0.75 + 0.3045(2d - d_1 - d_2)], \dots (1)$$

where  $d$ ,  $d_1$ , and  $d_2$  are the measured densities of the mixture, pure carbon tetrachloride and pure acetonitrile respectively.

### III. LIQUID-VAPOUR EQUILIBRIUM DATA

The liquid-vapour equilibrium data are shown in Table 4, where  $x_1$  and  $y_1$  are the mole fractions of carbon tetrachloride in the liquid and vapour respectively,  $P$  is the total pressure in standard mm Hg, and  $\alpha$  is the relative volatility given by  $\alpha = (y_1 x_2)/(y_2 x_1)$ .

TABLE 4  
CARBON TETRACHLORIDE + ACETONITRILE AT 45.00 °C  
Experimental data and derived functions

$x_1$	$y_1$	$P$	$\alpha$	$\mu_1^E$	$\mu_2^E$	$G_x^E$
0.0347	0.1801	247.96	6.112	1032	1.9	37.6
0.0892	0.3309	291.58	5.051	916.8	9.3	90.2
0.1914	0.4603	335.99	3.604	727.0	35.7	168.0
0.2887	0.5129	355.85	2.595	569.6	87.8	226.9
0.3752	0.5429	364.57	1.978	453.9	145.1	261.0
0.4567	0.5633	368.82	1.535	359.5	212.3	279.5
0.4790	0.5684	369.62	1.432	336.2	232.9	282.4
0.5060	0.5740	370.23	1.315	308.6	259.5	284.3
0.6049	0.5936	371.09	0.9542	217.7	373.3	279.2
0.7164	0.6181	368.95	0.6406	131.9	541.4	248.0
0.8069	0.6470	362.78	0.4386	74.3	726.0	200.1
0.8959	0.7004	346.97	0.2716	29.3	989.1	129.2
0.9609	0.8001	314.43	0.1629	6.2	1298	56.7

These data show that an azeotrope is formed at 45.00 °C having a mole fraction of carbon tetrachloride of 0.590 and at a total pressure of 371.2 mm Hg.

### IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials  $\mu_1^E$  and  $\mu_2^E$  and the excess free energy of mixing  $G_x^E$  were calculated from the equilibrium data using equations (2), (3), and (4) of Brown and Smith (1954). The values obtained (cal/g-mol) are shown in Table 4. Values of the liquid molar volumes and second virial coefficients at 45 °C in the equation of state for the vapours used in these calculations were obtained by the methods described by Brown and Smith (1954), they are :

$$\begin{array}{cccccc} \beta_{11} & \beta_{22} & \beta_{12} & \delta_{12} & V_1 & V_2 \\ -1.235 & -4.500 & -1.174 & +3.40 & 0.097 & 0.053 \end{array}$$

The excess free energy data at 45.00 °C were fitted by the method of least squares to equation (2)

$$G_x^E = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)^2 + d(x_1 - x_2)^3]. \quad \dots \quad (2)$$

The values of the constants and the standard deviation  $\sigma$  of the fit were (in cal/g-mol):

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	$\sigma$
Four constant equation	+1134.3	+118.9	+162.2	+99.5	1.1

Values of the second derivative of the total free energy of mixing with respect to  $x_1$  were also calculated and these gave no change of sign, showing that equation (2) with the above values of the constants does not indicate separation into two liquid phases.

The method of Herington (1947) and Redlich and Kister (1948) was used to test the thermodynamic consistency of the results which was shown to be satisfactory as the ratio of the areas above and below datum in a plot of  $\mu_1^E - \mu_2^E$  against  $x_1$  was 1.032.

The errors in  $G_x^E$  due to the errors in the measured quantities were estimated to be of the order of 2.2 cal/mole of which approximately half is due to uncertainty in the estimated value of the virial coefficients of the vapours and their mixture.

## V. CONCLUSIONS

Thermodynamically consistent values are given for the liquid-vapour equilibrium and excess free energy of mixing for the system carbon tetrachloride + acetonitrile at 45.00 °C. These data will be used to calculate the excess entropy of mixing for this system as soon as heat of mixing measurements have been completed. This system forms an azeotrope at 45.00 °C having a mole fraction of carbon tetrachloride of 0.590 and a total pressure of 371.2 mm Hg.

## VI. ACKNOWLEDGMENT

The authors thank Mr. O. H. Rigby for his help in the purification of the components.

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# THE ALKALOIDS OF *EVODIA LITTORALIS* ENDL.

By R. G. COOKE\* and H. F. HAYNES\*

[Manuscript received April 15, 1954]

## Summary

The bark and leaves of *Evodia littoralis* Endl. contain dictamnine, kokusaginine, and a new furoquinoline alkaloid, evolitrine. Hydrogenolysis of *isoevolitrine* yields 1-methyl-3-ethyl-4-hydroxy-7-methoxy-2(1H)-quinolone, which has been synthesized by two routes. Assuming the usual linear structure, evolitrine must be 7-methoxydictamnine.

## I. INTRODUCTION

Several species of *Evodia* are known to contain alkaloids and a survey of Australian species is in progress (Webb 1948, 1949, 1952; Hughes and Neill 1949; Eastwood, Hughes, and Ritchie 1954). Chemical investigation of *Evodia littoralis* Endl. has been reported by Lahey and Jones (1939) but the material is now known to have come from *E. vitiflora* F. Muell. and the former species is apparently confined to Norfolk Island (L. S. Smith, personal communication). Bark and leaves of *E. littoralis* have now been obtained from this source and we report the isolation of dictamnine, kokusaginine, and a new furoquinoline alkaloid, evolitrine.

## II. IDENTIFICATION OF THE ALKALOIDS

Dictamnine, the simplest of the furoquinoline alkaloids, was first isolated by Thoms (1923) from *Dictamnus albus* L., and subsequently from *Skimmia repens* Nakai by Asahina, Ohta, and Inubuse (1930), who determined the structure. Although several new furoquinoline alkaloids have been isolated recently from Australian plants, this simplest representative has not been found with them. The alkaloid isolated from *E. littoralis* was identified by preparation of derivatives and by direct comparison with an authentic specimen isolated by Asahina and co-workers, and kindly supplied by Professor Shoji Shibata. The alkaloid was also hydrogenated to a dihydro-derivative.

Kokusaginine was first isolated by Terasaka (1933), but during the present Australian phytochemical survey it has been found in *E. xanthoxyloides* F. Muell. by Hughes and Neill (1949), in *Flindersia collina* Bail. by Anet *et al.* (1952), who determined the structure, and in *Acronychia baueri* Schott. by Lamberton and Price (1953a). The material obtained from *E. littoralis* was identified by direct comparison with an authentic sample.

Evolitrine,  $C_{13}H_{11}O_3N$ , contains two methoxyl groups but no methylimino-group. It is readily isomerized to *isoevolitrine*, which contains only one methoxyl

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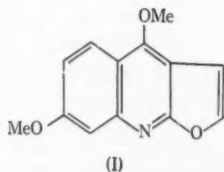
and one methylimino-group. The ultraviolet absorption spectrum so closely resembles that of kokusaginine that an analogous structure seems certain, and evolitrine is therefore presumably a methoxydictamnine.

Of the possible positions for the extra methoxyl group, the 8-position is probably excluded because evolitrine is very different from  $\gamma$ -fagarine. The 6-position is excluded because *isoevolitrine* is not identical with the compound obtained by Lamberton and Price (1953b) as a degradation product from medicosmine.

As evolitrine was available in only small quantity the usual degradation to a 2,4-dihydroxyquinoline by oxidation, demethylation, and decarboxylation seemed impracticable. The alkaloid was therefore converted to *isoevolitrine*, which was subjected to hydrogenolysis, a tetrahydro-derivative being formed. It is known that 3-ethylquinolones may be obtained in this way, and Ohta and Miyazaki (1953) have suggested this procedure as an alternative method for determining the structures of furoquinoline alkaloids when only small amounts are available.

The 7-position seemed the most likely location for the methoxyl group in evolitrine, so 1-methyl-3-ethyl-4-hydroxy-7-methoxy-2(1H)-quinolone was synthesized. Condensation of *m*-anisidine and diethyl ethyl malonate gave the monoanilide, which was cyclized to the dihydroxyquinoline. Methylation with dimethyl sulphate and alkali gave an oil which was readily hydrolysed to the required quinolone with hydrochloric acid. The alternative route, starting with 2-nitro-4-methoxybenzoyl chloride and diethyl ethyl malonate, was less satisfactory. The product from these syntheses was identical with the tetrahydro-derivative obtained by hydrogenolysis of *isoevolitrine*.

Assuming the linear furoquinoline structure which has been established for both dictamnine and kokusaginine, evolitrine must be 7-methoxydictamnine (I).



### III. EXPERIMENTAL

Melting points are corrected. Light petroleum refers to a fraction of boiling range 40–70 °C. Microanalyses by Dr. W. Zimmermann and assistants.

(a) *Extraction of the Leaves.*—The milled, air-dry leaves (5.36 kg; 10.7% moisture) were extracted with methanol in a Soxhlet apparatus, the solvent was removed, and the viscous dark green residue was boiled repeatedly with hydrochloric acid (2%) until all basic material had been removed. The acid extracts were combined, filtered, basified with ammonia, and extracted exhaustively with chloroform. The chloroform extract was washed with aqueous sodium hydroxide (2%) and then with water. The washings contained only traces of organic matter and were discarded. Evaporation of the chloroform left a dark brown residue which was dissolved in acetone. Addition of concentrated hydrochloric acid precipitated the hydrochlorides, which

were filtered and washed well with acetone. No more basic material could be recovered from the acetone mother liquor and washings. Basification of the hydrochlorides gave a crystalline product which was dissolved in benzene and passed over a column of alumina. Elution with benzene gave a mixture of two alkaloids separated by fractional crystallization from aqueous ethanol and further chromatography of the more soluble fraction to give dictamnine (310 mg, m.p. 130–131 °C) and evolitrine (70 mg, m.p. 97–99 °C).

The third alkaloid was eluted from the first alumina column by benzene containing 0.5% by volume of ethanol. Evaporation gave kokusaginine (30 mg, m.p. 165–166 °C).

(b) *Extraction of the Bark*.—The milled air-dry bark (1.35 kg; 9.6% moisture) was treated with lime (400 g), and the mixture was moistened thoroughly with water and allowed to dry in the air. The material was then extracted with trichloroethylene by percolation at room temperature. The combined extracts were evaporated and the residual dark brown gum was extracted repeatedly with boiling hydrochloric acid (5%). The three bases were then isolated as described above, giving dictamnine (60 mg), evolitrine (42 mg), and kokusaginine (14 mg).

(c) *Dictamnine*.—Further crystallization from aqueous ethanol gave fine needles, m.p. 132–133 °C alone or mixed with authentic dictamnine. The two samples both had  $R_F$  0.89 in butanol-5% acetic acid (Found: C, 72.6; H, 4.5; N, 7.3; OMe, 15.6%. Calc. for  $C_{12}H_{11}O_2N$ : C, 72.4; H, 4.6; N, 7.0; OMe, 15.5%).

The picrate formed yellow plates from methanol, m.p. 164–165 °C (lit. 163 °C).

By heating with excess methyl iodide in a sealed tube for 4 hr at 100 °C dictamnine was converted to isodictamnine which crystallized from water in silky needles, m.p. 187–188 °C (lit. 188 °C).

(d) *Hydrogenation of Dictamnine*.—The base was hydrogenated in ethanol over Pd/C (20%) at room temperature and pressure. The product was purified by chromatography of a benzene solution on alumina, followed by crystallization from aqueous methanol. The dihydrodictamnine formed needles, m.p. 103–104 °C (Found: C, 71.2; H, 5.4%. Calc. for  $C_{14}H_{11}O_2N$ : C, 71.6; H, 5.5%).

The picrate separated from ethanol as yellow needles, m.p. 189–189.5 °C (Found: C, 50.2; H, 3.2%. Calc. for  $C_{12}H_{11}O_2N.C_6H_5O_7N_3$ : C, 50.2; H, 3.3%).

(e) *Kokusaginine*.—The base crystallized from benzene in prisms, m.p. 170–171 °C not depressed by mixing with authentic kokusaginine. The  $R_F$  values of the two samples in butanol-5% acetic acid were 0.83 and 0.82 respectively (Found: C, 64.9; H, 4.9; N, 5.4%. Calc. for  $C_{14}H_{13}O_4N$ : C, 64.9; H, 5.1; N, 5.4%). The picrate crystallized from ethanol as yellow needles, m.p. 216–217 °C (decomp.) not depressed by the authentic picrate. The hydrochloride separated from hydrochloric acid (2%) in needles, m.p. 224 °C (decomp.) (lit. m.p. 224 °C (decomp.)).

(f) *Evolitrine*.—The base crystallized from light petroleum in rosettes of needles, m.p. 114–115 °C (Found: C, 68.1; H, 4.6; N, 6.1; NMe, nil; OMe, 25.3%. Calc. for  $C_{13}H_{11}O_2N$ : C, 68.1; H, 4.6; N, 6.1; 2×OMe, 27.1%). Light absorption in ethanol (95%):  $\lambda_{max}$ , m $\mu$  246.5, 256, 290, 300, 307.5, 319, 332.5; log  $\epsilon_{max}$ , 4.81, 4.28, 3.73, 3.88, 3.97, 3.96, 3.87 (italicized values indicate inflexions).

The picrate crystallized from ethanol as yellow needles, m.p. 191–192 °C (Found: C, 49.9; H, 3.2; N, 12.6; OMe, 13.2%. Calc. for  $C_{13}H_{11}O_3N.C_6H_5O_7N_3$ : C, 49.8; H, 3.1; N, 12.2; 2×OMe, 13.5%).

The hydrochloride was prepared in acetone solution and crystallized from ethanol-ether in rods, m.p. 150–151 °C (decomp.). It slowly hydrolysed in aqueous solution, regenerating evolitrine (m.p. and mixed m.p.).

(g) *isoEvolitrine*.—Treatment of evolitrine with methyl iodide as described for dictamnine gave isoevolitrine, which formed needles from water, m.p. 193–194 °C, and became pink on exposure to light (Found: OMe, 11.9; (N)Me, 3.8%. Calc. for  $C_{13}H_{11}O_2N$ : 1×OMe, 13.5; 1×(N)Me, 6.6%).



(h) *Hydrogenolysis of isoEvolitrine*.—The compound was dissolved in ethanol and treated with hydrogen and Adams's catalyst at room temperature and pressure. The resulting 1-methyl-3-ethyl-4-hydroxy-7-methoxy-2(1H)-quinolone crystallized from aqueous ethanol in needles, m.p. 223–224 °C, not depressed by mixing with a synthetic specimen (see below). The compound is readily soluble in aqueous sodium hydroxide (5%) but is insoluble in boiling hydrochloric acid (5%) (Found: C, 67.2; H, 6.2%. Calc. for  $C_{13}H_{15}O_3N$ : C, 67.0; H, 6.5%).

(i) *Synthesis of 1-Methyl-3-ethyl-4-hydroxy-7-methoxy-2(1H)-quinolone*.—Diethyl ethyl malonate (3.3 g) and *m*-anisidine (2.0 g) were heated together on the water-bath for 4 hr. The resultant dark brown oil was added dropwise to refluxing "Dowtherm" (20 ml) and heating was then continued for 10 min. On cooling the mixture, 3-ethyl-7-methoxy-2,4-dihydroxyquinoline separated and was filtered and washed with light petroleum. Dilution of the "Dowtherm" mother liquor with light petroleum gave more of the product. Total yield 68%. The product crystallized from methanol in prisms, m.p. 260–261 °C (Found: C, 65.8; H, 6.0; N, 6.6%. Calc. for  $C_{12}H_{13}O_3N$ : C, 65.8; H, 6.0; N, 6.4%).

This compound was methylated with dimethyl sulphate and aqueous sodium hydroxide (20%) and the resulting oil was refluxed with hydrochloric acid (5N) for 2 hr. The solid was filtered from the cooled mixture and dissolved in dilute aqueous alkali. Acidification of the filtered solution gave 1-methyl-3-ethyl-4-hydroxy-7-methoxy-2(1H)-quinolone which crystallized from aqueous ethanol in needles, m.p. 223–224 °C, alone or mixed with the hydrogenolysis product from *isoevolitrine* (Found: C, 67.3; H, 6.4; N, 5.95; OMe, 13.2; (N)Me, 6.7%. Calc. for  $C_{13}H_{15}O_3N$ : C, 67.0; H, 6.5; N, 6.0; 1×OMe, 13.6; 1×(N)Me, 6.4%).

This compound was also prepared as follows: 2-nitro-4-methoxybenzoyl chloride was condensed with the ethoxy magnesium derivative of diethyl ethyl malonate. The resulting keto-ester was heated with tin and hydrochloric acid but the 2,4-dihydroxyquinoline derivative could not be separated from the resulting tin complex. The mixture was treated with excess sodium hydroxide and dimethyl sulphate and the small quantity of oil formed was hydrolysed with hydrochloric acid (5N) to give the same product (m.p. and mixed m.p.) as in the preceding synthesis.

#### IV. ACKNOWLEDGMENTS

We are indebted to officers of C.S.I.R.O. and the Department of External Territories for arranging the collection of plant material. We also thank Professor Shoji Shibata, University of Tokyo, for authentic dictamnine, Dr. J. R. Price, C.S.I.R.O., for authentic kokusaginine, and Mr. L. S. Smith, Queensland Herbarium, for botanical information.

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# THE ALKALOIDS OF *HELIOTROPIUM EUROPAEUM* L.

## I. HELIOTRINE AND LASIOCARPINE

By C. C. J. CULVENOR,\* L. J. DRUMMOND,\* and J. R. PRICE\*

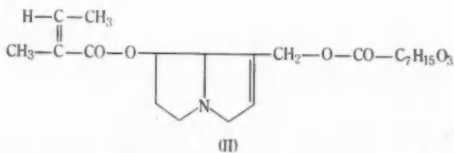
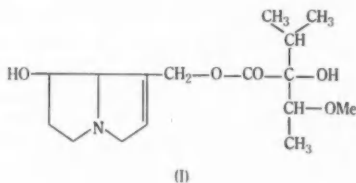
[Manuscript received April 9, 1954]

### Summary

The chief crystalline bases of *Heliotropium europaeum* L. are heliotrine and lasiocarpine. Three other bases are present, one in major amount, as also are the *N*-oxides of all five alkaloids. A method of assay has been developed, based on partition chromatography, which permits the estimation of each of the 10 constituents in plant material.

### I. INTRODUCTION

*Heliotropium europaeum* L. is a summer annual herb, abundant on fallow land in certain areas of New South Wales, Victoria, and South Australia. Its consumption by sheep leads to a disease which is frequently fatal and of which liver damage is a characteristic feature (Annual Reports of the Toxaemic Jaundice



Investigation Committee 1947-48, 1948-49). In view of the similarity to the effect of certain *Senecio* alkaloids, a preliminary examination was made by Trautner and Neufeld (1949) who isolated two alkaloids resembling heliotrine (I) and lasiocarpine (II) which had been reported previously from *H. lasiocarpum* (Menshikov 1932). The objects of the present work were to confirm the identifications of Trautner and Neufeld, to determine what other alkaloids may be present, and to devise a method for estimating the quantities of each alkaloid

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in order to study seasonal and local variations. Since the work commenced, a report by Russian workers has appeared dealing with the hepatotoxic properties of *H. lasiocarpum* (Bourkser 1947).

The properties of the principal alkaloid isolated by Trautner and Neufeld ("isoheliotrine") differed from those of heliotrine only in respect of the optical rotation which was found to be  $+49.3^\circ$  compared with  $-75^\circ$  for heliotrine. The properties, including optical rotation, of the hydrolysis products were the same as those reported for heliotridine and heliotric acid. The minor alkaloid was not examined in detail but its melting point, rotation, molecular weight, and solubility all pointed to identity with lasiocarpine. We have repeated the

TABLE I  
SPECIFIC ROTATION OF HELIOTRINE IN VARIOUS SOLVENTS

Solvent	Concentration, c	Specific Rotation, [ $\alpha$ ] <sub>D</sub> <sup>17</sup>
Chloroform .. .. .	10.50	+54.2
" .. .. .	5.22	+59.4
" .. .. .	2.10	+62.4
" .. .. .	1.05	+63.8
Ethanol .. .. .	4.82	+17.6
Hydrochloric acid (0.27N)	5.29	-10.4
Sulphuric acid (2N) .. ..	10.59	-11.3
" .. .. .	5.30	-12.5
" .. .. .	1.06	-14.2

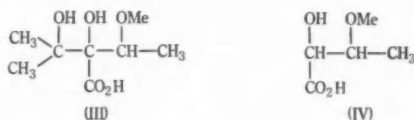
work of Trautner and Neufeld and by further study of the degradation products have established that the principal alkaloid from *H. europaeum* is identical with heliotrine in all respects reported by Menshikov, except as regards rotation. The hydroxyheliotridane obtained by hydrogenolysis has substantially the same properties as those reported by Menshikov, but is obviously not homogeneous and is evidently a mixture of the two possible isomers resulting from hydrogenation of the double bond. The situation is thus different from that obtaining with retronecine and retronecine esters, hydrogenolysis of which gives rise to one isomer only (Adams and Leonard 1944).

Since the hydrolysis and hydrogenolysis products are the same, it follows that the alkaloid of *H. europaeum* is not an optical isomer of, but is identical with heliotrine. The specific rotation,  $-75^\circ$ , given by Menshikov is apparently an error. We find the specific rotation of heliotrine in chloroform to be similar to that reported by Trautner and Neufeld, values at different concentrations and in other solvents being shown in Table 1.

The identification of the second alkaloid as lasiocarpine has likewise been confirmed, although the hydroxyheliotridane obtained by hydrogenolysis followed by hydrolysis is again a mixture of the two isomers, in somewhat different proportions, as judged by the rotation, from those obtaining in the heliotrine product. It has been shown that lasiocarpic acid, the acid liberated



by hydrogenolysis of lasiocarpine, is 2,3-dihydroxy-4-methoxy-2-methylpentane-3-carboxylic acid (III) (Drummond 1951). This structure was based on the following evidence: (i) the molecule contained one methoxyl and two hydroxyl groups, (ii) oxidation with periodate gave rise to acetone with consumption of 1 mole of periodate, (iii) a yellow ferric reaction and the evolution of carbon monoxide with sulphuric acid indicated an  $\alpha$ -hydroxy acid, and (iv) Kuhn-Roth oxidation gave 1.57 moles acetic acid, a similar value being found for heliotric acid. Lasiocarpic acid readily yields acetone on heating in dilute alkali and the reaction mixture also contains an acid  $C_5H_{10}O_4$  presumably 2-hydroxy-3-methoxybutanoic acid (IV), which was isolated as its *p*-phenylphenacyl ester. An acid of the structure IV has been synthesized in racemic form by Dry and Warren



(1953), but the melting point of the derived *p*-phenylphenacyl ester differs from that of the lasiocarpic acid degradation product. The periodate oxidation of lasiocarpic acid may apparently proceed further than the initial glycol fission since it was recently observed (Bradbury, personal communication) that when the procedure of Jackson (1944) is used, 2 moles of periodate are consumed.

Paper chromatograms of the crude alkaloidal extracts, run with butanol-acetic acid, showed five spots printed by iodine with  $R_F$  values 0.28, 0.42, 0.52, 0.59, and 0.69. Two of these were due to heliotrine ( $R_F$  0.42) and lasiocarpine ( $R_F$  0.59), but first attempts to isolate other constituents from mother liquors were not successful. Since examples of the co-occurrence of pyrrolizidine alkaloids with their *N*-oxides were already known (Menshikov and Borodina 1945; Christie *et al.* 1949) the presence of *N*-oxides was suspected. Heliotrine and lasiocarpine *N*-oxides were prepared and found to have  $R_F$  values 0.52 and 0.69 respectively. Confirmatory evidence for their existence in the plant was obtained by reduction of the aqueous liquors after extraction of the crude bases with chloroform; re-extraction then gave substantial additional amounts of both heliotrine and lasiocarpine (both *N*-oxides have since been isolated directly from the plant, see Part II of this series (Culvenor 1954)). Koekemoer and Warren (1951) have since demonstrated the occurrence of *N*-oxides in several *Senecio* species, and their prediction that *N*-oxides are probably widespread in other genera containing pyrrolizidine alkaloids has already been substantiated by the present authors with other members of the Boraginaceae, and with several *Crotalaria*, *Senecio*, and *Erechtites* species (unpublished data).

In isolating the alkaloids of *H. europaeum*, the aqueous acid extract is reduced before extracting the bases after the manner of Koekemoer and Warren (1951). This reduction should be carried out with zinc dust and acid rather than with sulphur dioxide since only a very low yield of lasiocarpine, if any, is obtained from lasiocarpine *N*-oxide using the latter reagent. The reaction of

amine oxides with sulphur dioxide may give two types of adduct, only one of which hydrolyses to the parent tertiary amine; the other adduct yields a secondary amine and an aldehyde (Burg 1943; Lecher and Hardy 1948). The latter adduct probably predominates with lasiocarpine *N*-oxide although it has not been possible to purify the main reaction product. Heliotrine *N*-oxide, on the other hand, is reduced to heliotrine in good yield by sulphur dioxide. Since the *N*-oxides of heliotrine and lasiocarpine (and also of several other pyrrolizidine alkaloids which have been examined) have  $R_F$  values approximately 0.1 higher than the free bases, heliotridine *N*-oxide was prepared in case it should be the unknown base of  $R_F$  0.28 (heliotridine has  $R_F$  0.16). However, heliotridine *N*-oxide has  $R_F$  0.22 and it was shown that the compound  $R_F$  0.28 cannot be an *N*-oxide since it is present in reduced extracts.

TABLE 2  
ALKALOID  $R_F$  VALUES IN BUTANOL-ACETIC ACID AND BUTANOL-AMMONIA

Alkaloid	BuOH-AcOH	BuOH-NH <sub>3</sub>
Heliotrine .. .. .	0.42	0.85
Lasiocarpine .. .. .	0.59	0.90
Base C .. .. .	0.48	0.90
Base F .. .. .	0.37	0.86
Base G .. .. .	0.28	0.78
Heliotridine .. .. .	0.16	0.61
Lasiocarpine <i>N</i> -oxide ..	0.69	0.70
Heliotrine <i>N</i> -oxide .. ..	0.52	0.52
Base G <i>N</i> -oxide .. ..	0.37	0.33
Heliotridine <i>N</i> -oxide ..	0.22	0.15

Two simple distinguishing tests for amine oxides have been used in the present work and have so far proved reliable. The first is the colour reaction of amine oxides with acetic anhydride (Polonovski and Polonovski 1926), and the second is based on the observation that the  $R_F$  values of *N*-oxides are altered only very slightly, if at all, when butanol-ammonia is substituted for butanol-acetic acid as chromatographing solvent, whereas the tertiary amines have much higher  $R_F$  values in the basic solvent. Typical  $R_F$  values for the various alkaloids and *N*-oxides are recorded in Table 2 (see also Section III).

## II. ESTIMATION OF THE ALKALOIDS

The method of estimating the concentration of a solute on a paper chromatogram by means of the empirical relation between spot area and amount of substance applied (Fisher, Parsons, and Morrison 1948; Fisher and Holmes 1949) proved reasonably satisfactory for heliotrine and lasiocarpine in solutions of the pure bases, but with crude plant extracts resolution and definition of the spots was too poor to allow estimation of even the three major bases in this way. Other developing solvents and printing reagents were tried but gave no better results. However, a good separation of the alkaloids, even in crude extracts, is obtained by chromatography on columns of kieselguhr buffered at pH 8.0,

using a series of eluting solvents as in the method employed by Bottomley and Mortimer (1954) for estimating the tropane alkaloids in *Duboisia* species. Partition chromatography in this form has revealed the presence of at least two minor alkaloids previously unrecognized and has now been made the basis of an assay procedure for determining all five bases and their *N*-oxides in

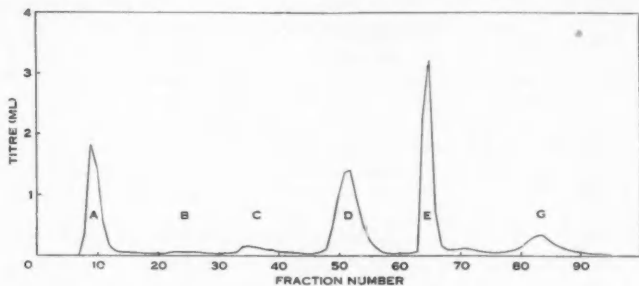


Fig. 1.—Separation of the "unreduced" alkaloids of *H. europaeum* on kieselguhr-pH 8.0 buffer.

*H. europaeum*. Since the *N*-oxides are difficult to extract from aqueous solution with chloroform and, apart from lasiocarpine *N*-oxide, are not eluted from the partition column under the conditions employed, they are estimated indirectly by determining the tertiary bases before and after reduction of the crude alkaloid extracts.

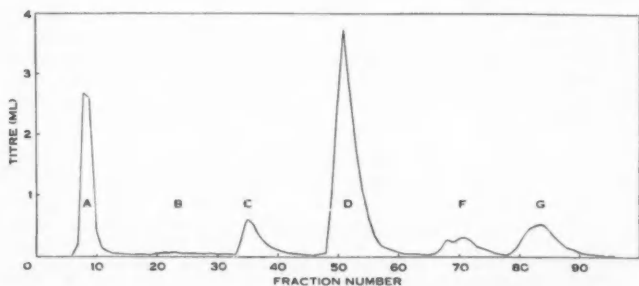


Fig. 2.—Separation of the "reduced" alkaloids of *H. europaeum* on kieselguhr-pH 8.0 buffer.

Typical elution curves for "unreduced" and "reduced" alkaloids are shown in Figures 1 and 2 respectively. The identity of the base in each peak was established by recovery from appropriately combined fractions and determination of  $R_F$  values. This also provides a check on the efficiency of the separation since the presence of more than one base in a peak is immediately evident. The bases present in the various peaks are as follows: peak A, lasiocarpine; peak B, partly lasiocarpine and partly unidentified bases; peak C, new minor alkaloid (base C); peak D, heliotrine; peak E, lasiocarpine *N*-oxide; peak F,

new minor alkaloid (base *F*) ; peak *G*, unknown base *G*. The  $R_F$  values of the new bases are shown in Table 1. Assay results for samples of *H. europaeum* seed and whole plant are given in Tables 3 and 4. The ratio of free base to *N*-oxide and the amount of "total" base (i.e. free base + *N*-oxide) show considerable variation in different plant samples but the individual alkaloids have always

TABLE 3  
ASSAY OF THE WHOLE PLANT OF *H. EUROPAEUM*

Alkaloid	Free Base (% dry wt.)	<i>N</i> -Oxide (% dry wt.)
Lasiocarpine .. ..	0.037	0.26
Base <i>C</i> .. ..	—	0.02
Heliotrine .. ..	0.026	0.26
Base <i>F</i> .. ..	—	0.018
Base <i>G</i> .. ..	0.027	0.11

been present in similar proportions. Thus lasiocarpine, heliotrine, and base *G* are always the major, bases *C* and *F* always the minor constituents. A sample of *H. europaeum* from Portugal had essentially the same alkaloid composition as the Australian plant. The constitutions of bases *C*, *F*, and *G* are discussed in Part II (Culvenor 1954).

TABLE 4  
ASSAY OF THE SEED OF *H. EUROPAEUM*

Alkaloid	Free Base (% dry wt.)	<i>N</i> -Oxide (% dry wt.)
Lasiocarpine .. ..	0.014	0.36
Base <i>C</i> .. ..	—	0.11
Heliotrine .. ..	0.027	0.74
Base <i>F</i> .. ..	—	0.08
Base <i>G</i> .. ..	0.014	0.40

### III. EXPERIMENTAL

All melting points are corrected except where otherwise stated. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Extraction of the Alkaloids*.—No procedure was rigidly adhered to but the essential features of the extractions were as follows. Milled whole plant was exhaustively extracted with methanol, the extracts evaporated under reduced pressure and the residue extracted four times with aqueous hydrochloric acid (1%). The combined acid solutions were divided into two portions, the first portion basified with sodium carbonate and the crude alkaloid shaken out with chloroform. Paper chromatograms of a number of such crude alkaloid fractions run with butanol-5% acetic acid showed the presence of up to five components with  $R_F$  values 0.28, 0.42, 0.52, 0.59, and 0.69. All five were not present in every sample in sufficient concentration to show up on chromatograms. The second portion of the acid extracts, after addition of sulphuric acid to a concentration of approximately 2*N*, was kept with intermittent shaking with zinc dust for 24 hr. The solution was filtered, basified with ammonia, and the alkaloid extracted with chloroform. Paper chromatograms (butanol-acetic acid) of these crude "reduced" bases

showed three spots with  $R_F$  values 0.28, 0.42, and 0.59. Extraction of the crude alkaloids, "reduced" or "unreduced", with boiling light petroleum gave lasiocarpine; crystallization of the light petroleum-insoluble material from acetone gave heliotrine. The yields of the two alkaloids varied considerably, and whereas both bases were always present after reduction, from some samples lasiocarpine was the only base isolated before reduction.

(b) *Lasiocarpine*.—Lasiocarpine crystallized from light petroleum as colourless plates, m.p. 96.5–97 °C,  $[\alpha]_D^{16}$   $-3.5^\circ$ ,  $-3.3^\circ$ ,  $-3.0^\circ$  (c, 20.0, 10.0, and 5.0 respectively in ethanol),  $+0.9^\circ$  (c, 6.3 in chloroform) (Found: C, 61.3; H, 8.3; N, 3.4;  $\text{CH}_3\text{O}$ , 8.0%. Calc. for  $\text{C}_{21}\text{H}_{33}\text{O}_5\text{N}$ : C, 61.3; H, 8.0; N, 3.4;  $\text{CH}_3\text{O}$ , 7.5%).  $R_F$  values: butanol-5% acetic acid, 0.59; butanol-ammonia, 0.90. Alkaline hydrolysis gave angelic acid, m.p. 44–45 °C and heliotridine (yield 93%), m.p. 117.5–118 °C,  $[\alpha]_D^{16} +33^\circ$  (c, 9.0 in methanol), hydrochloride, m.p. 122–124 °C (Found (for heliotridine): O, 20.2; N, 8.8%. Calc. for  $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$ : O, 20.6; N, 9.0%). Lasiocarpine was hydrogenolysed by shaking a solution of the alkaloid (15.0 g) in hydrochloric acid (0.5N; 90 ml) containing chloroplatinic acid (500 mg) and platinum oxide (5 mg) with hydrogen under a pressure of 3 atm for 12 hr. Extraction of the filtered solution with ether gave an acid (6.8 g); basification and re-extraction with ether gave a basic ester, b.p. 135–136 °C/8 mm,  $R_F$  (butanol-acetic acid) 0.68,  $[\alpha]_D^{17} +4.2^\circ$ ,  $+4.3^\circ$ ,  $+4.4^\circ$  (c, 10.1, 5.35, and 2.7 respectively in ethanol), picrate, long yellow needles, m.p. 165–166 °C. Menshikov and Schdanovich (1936) report b.p. 123–125 °C/8 mm and  $[\alpha]_D +3.8^\circ$  for the basic ester obtained by hydrogenolysis of lasiocarpine, and m.p. 157–159 °C for its picrate. The acid (yield 97%) had m.p. 96–97 °C and  $[\alpha]_D^{18} +8.4^\circ$  (c, 4.18 in ethanol) (Found: C, 50.2; H, 8.4;  $\text{CH}_3\text{O}$ , 16.2;  $\text{CH}_3(\text{C})$ , 12.2, 12.4%. Calc. for  $\text{C}_9\text{H}_{13}\text{O}_3$ : C, 50.0; H, 8.4;  $\text{CH}_3\text{O}$ , 16.1;  $\text{CH}_3(\text{C})$ , 7.8% (one  $\text{CH}_3(\text{C})$  group)). Lasiocarpic acid (Menshikov and Schdanovich 1936) has m.p. 95–97 °C and  $[\alpha]_D +10.6^\circ$ . In a small-scale experiment 1.5 g lasiocarpine took up 275.6 ml  $\text{H}_2$  at 20 °C/776 mm. Calc. for 3 moles  $\text{H}_2$ , 263.2 ml.

Alkaline hydrolysis of the basic ester gave an acid, b.p. 174–176 °C (2-methylbutanoic acid; yield quantitative) and a base which partially crystallized at room temperature. It had  $[\alpha]_D^{18} +0.5^\circ$  (c, 19.15 in water), b.p. 130 °C/7 mm and, after distillation, m.p. 56–58 °C,  $[\alpha]_D^{18} +0.2^\circ$  (c, 10.88 in water), and  $R_F$  (butanol-acetic acid) 0.30 (Found: C, 68.0; H, 10.7; N, 10.4%. Calc. for  $\text{C}_9\text{H}_{13}\text{ON}$ : C, 68.1; H, 10.6; N, 9.9%. The picrate, after four crystallizations from ethanol, melted at 200–201 °C (Found: C, 45.7; H, 5.0%. Calc. for  $\text{C}_{14}\text{H}_{19}\text{O}_6\text{N}_4$ : C, 45.4; H, 4.9%). According to Menshikov (1935), hydroxyheliotridane has m.p. 61–65 °C, b.p. 126–128 °C/12 mm, and  $[\alpha]_D -14.5^\circ$ . It forms a picrate, m.p. 196 °C and a methiodide, m.p. 296 °C.

Some difficulty was experienced with the hydrogenolysis of lasiocarpine using platinum oxide alone as catalyst, anomalous results being obtained with some batches of catalyst. The yield of lasiocarpic acid was low, varying from 55–78% and the basic fraction, the yield of which was correspondingly higher than expected, was a viscous high boiling oil.

(c) *Lasiocarpine N-Oxide*.—A solution of lasiocarpine (40 g) in ethanol (150 ml) was mixed with hydrogen peroxide (30%; 40 ml) and kept for 2 days at room temperature, after which excess hydrogen peroxide was destroyed by the addition of small amounts of manganese dioxide with intermittent shaking until gas evolution ceased. The mixture was filtered, the filtrate evaporated *in vacuo*, and the residue crystallized from acetone to give the *N-oxide* (18.2 g) as colourless prisms or needles, m.p. 124–126 °C. Recrystallization from ethyl acetate or from acetone-methanol raised the m.p. to 134–135 °C (decomp.), although apparently equally pure samples may melt at any point between this and 129–130 °C (decomp.). The variability of the m.p. is probably related to the difficulty of removing all solvent of crystallization without decomposing the compound (Found (sample crystallized from acetone-methanol and dried 3 hr *in vacuo* at 80 °C): C, 57.7; H, 8.0; N, 3.4%; equiv. wt. 443; (the same sample after drying a further 5 hr *in vacuo* at 100 °C and becoming light brown in colour): C, 57.2; H, 8.1; N, 2.8%; equiv. wt. 445; (sample crystallized from ethyl acetate, dried 3 hr at 80 °C *in vacuo*, m.p. 132 °C (decomp.): C, 58.1; H, 8.1; N, 3.18%. Calc. for  $\text{C}_{21}\text{H}_{33}\text{O}_6\text{N}$ : C, 59.0; H, 7.8; N, 3.3%; equiv. wt. 427. Calc. for  $\text{C}_{21}\text{H}_{33}\text{O}_6\text{N.H}_2\text{O}$ : C, 56.6; H, 7.9; N, 3.2%; equiv. wt. 445;

$[\alpha]_D^{17} + 13.1^\circ$  (c, 4.97 in ethanol)). Lasiocarpine *N*-oxide is readily soluble in alcohols, chloroform, and hot benzene. Reduction with zinc dust and sulphuric acid gave an almost quantitative yield of lasiocarpine. The passage of sulphur dioxide into an ice-cold aqueous solution of lasiocarpine *N*-oxide (2 g) led to the rapid precipitation of an oil which later solidified. The crude product (1.8 g), which contained sulphur, had m.p. 144–148 °C, sintering from 140 °C, was readily soluble in acetone and ethanol, and separated from hot benzene on cooling either as a powder of virtually unchanged m.p., or as a glass. The solubilities and appearance changed considerably on attempted purification and no pure compound was isolated from the mixture. Hydrolysis of the crude  $\text{SO}_2$  adduct with alcoholic alkali at room temperature produced a gummy base which did not contain lasiocarpine.

(d) *Lasiocarpic Acid*.—(i) Lasiocarpic acid gave a yellow colour with  $\text{Fe}^{3+}$  and when heated at 140 °C with sulphuric acid (98%) evolved carbon monoxide, detected by passage through silica gel impregnated with palladium chloride.

(ii) Lasiocarpic acid (22.8 mg) was dissolved in sodium periodate solution (0.0278M; 20 ml), which had been adjusted to pH 4 with sulphuric acid, and 5 ml aliquots titrated after standing 1, 7, and 65 hr; 0.48, 0.98, and 1.0 moles periodate respectively were consumed per mole lasiocarpic acid. A solution of lasiocarpic acid (0.5 g) and sodium metaperiodate (1.2 g) in water (26 ml) and sulphuric acid (2.5N; 4 ml) was allowed to stand for 21 hr. Excess periodate was destroyed and the solution neutralized with sodium bicarbonate and distilled. The distillate contained acetone identified by means of its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic specimen 126–127 °C.

(iii) Lasiocarpic acid (2.0 g) was refluxed with aqueous potassium hydroxide (30%; 30 ml) for 2 days, small portions being distilled off and replaced by water at 2-hourly intervals as described by Lamberton and Price (1953) for noracronidine. The distillate contained acetone, isolated as the 2,4-dinitrophenylhydrazone (1.57 g), m.p. and mixed m.p. 126–127 °C after recrystallization. Heliotric acid under the same conditions gave no volatile carbonyl compound. The alkaline reaction mixture was acidified to Congo red and continuously extracted with ether giving 1.62 g oily acid. A paper chromatogram run with butanol-ammonia showed two spots, a major one  $R_F$  0.10 and a minor one  $R_F$  0.23 corresponding to lasiocarpic acid. The acid mixture was converted to the *p*-phenylphenacyl esters which when chromatographed on neutral alumina gave two crystalline esters in low yield. The first, believed to be *p*-phenylphenacyl 2-hydroxy-3-methoxybutanoate, was obtained as colourless needles from benzene-light petroleum, m.p. 115.5–116 °C (Found: C, 69.8; H, 6.1%. Calc. for  $\text{C}_{18}\text{H}_{20}\text{O}_6$ : C, 69.5; H, 6.0%). The second separated from aqueous ethanol as colourless needles, m.p. 143–144 °C (Found: C, 68.8; H, 6.8%. Calc. for  $\text{C}_{22}\text{H}_{24}\text{O}_6$ : C, 68.4; H, 6.7%). The *p*-phenylphenacyl ester of lasiocarpic acid was prepared for comparison and formed needles from aqueous ethanol, m.p. 145–145.5 °C (Found: C, 68.8; H, 6.9%. Calc. for  $\text{C}_{22}\text{H}_{24}\text{O}_6$ : C, 68.4; H, 6.7%); a mixture with the reaction product melted at 144–145 °C.

(e) *Heliotrine*.—Heliotrine crystallized from acetone as colourless prisms, m.p. 128 °C,  $[\alpha]_D^{17} + 54.2^\circ$  (c, 10.5 in chloroform), see also data in Table 1 (Found: C, 61.0; H, 8.4; N, 4.6; O, 26.1;  $\text{CH}_3\text{O}$ , 10.2%. Calc. for  $\text{C}_{18}\text{H}_{27}\text{O}_5\text{N}$ : C, 61.3; H, 8.6; N, 4.5; O, 25.6;  $\text{CH}_3\text{O}$ , 9.9%).  $R_F$  values: butanol-5% acetic acid, 0.42; butanol-ammonia, 0.85. The methiodide melted at 108–110 °C after softening at 103 °C. Heliotrine was recovered unchanged after refluxing with aqueous hydrochloric acid (2N) for 8 hr. Alkaline hydrolysis of heliotrine gave heliotridine (m.p. 117.5–118 °C alone or mixed with heliotridine from lasiocarpine,  $[\alpha]_D^{18} + 32^\circ$  (c, 10.0 in methanol)) and heliotric acid, m.p. 94–95 °C,  $[\alpha]_D^{18} - 12^\circ$  (c, 10.0 in water) (Found: C, 54.5; H, 9.0; O, 36.2;  $\text{CH}_3\text{O}$ , 17.5;  $\text{CH}_3(\text{C})$ , 13.6; 13.2%. Calc. for  $\text{C}_9\text{H}_{14}\text{O}_4$ : C, 54.5; H, 9.1; O, 36.4;  $\text{CH}_3\text{O}$ , 17.6; one  $\text{CH}_3(\text{C})$ , 8.5%).

Hydrogenolysis of heliotrine (10.0 g) under the conditions employed for lasiocarpine gave heliotric acid (5.54 g, 99%; m.p. and mixed m.p. with a specimen obtained by alkaline hydrolysis 94–95 °C,  $[\alpha]_D^{18} - 12.2^\circ$  (c, 10.0 in water)) and a base (4.22 g) which solidified at room temperature and had  $[\alpha]_D^{17} - 10.4^\circ$  (c, 16.88 in water). It had b.p. 132–133 °C/7 mm and, after distillation,

m.p. 51–56 °C and  $[\alpha]_D^{18} -10.7^\circ$  (c, 14.44 in water) (Found: C, 67.9; H, 10.6; N, 10.3%. Calc. for  $C_8H_{15}ON$ : C, 68.1; H, 10.6; N, 9.9%). When first prepared, the picrate melted about 190–195 °C, but after several recrystallizations from ethanol, had m.p. 200–201 °C (Found: C, 45.8; H, 4.9; N, 14.9%. Calc. for  $C_{14}H_{18}O_6N_4$ : C, 45.4; H, 4.9; N, 15.1%). The methiodide melted at 292 °C (uncorr.). Base recovered from the picrate of m.p. 200–201 °C had m.p. 59–60 °C,  $[\alpha]_D^{22} -11.1^\circ$  (c, 2.8 in water).

Oxidation of heliotric acid under the conditions described by Menshikov (1939) gave a liquid carbonyl compound, b.p. 132 °C,  $[\alpha]_D^{15} +20^\circ$ , semicarbazone, m.p. 146–147 °C.

(f) *Heliotrine N-Oxide*.—*Heliotrine N-oxide* prepared similarly to lasiocarpine *N-oxide*, separated from acetone-methanol in prisms, m.p. 171–172 °C,  $[\alpha]_D^{17} +26.6^\circ$  (c, 5.50 in ethanol) (Found: C, 58.1; H, 8.2; O, 28.9; N, 4.1%. Calc. for  $C_{14}H_{27}O_6N$ : C, 58.4; H, 8.3; O, 29.2; N, 4.3%). *Heliotrine* is obtained on reduction with either zinc and sulphuric acid (almost quantitatively) or with sulphur dioxide (85%).

(g) *Heliotridine N-Oxide*.—Prepared in the same way as other *N-oxides*, *heliotridine N-oxide* could be crystallized satisfactorily from acetone-methanol only by using large amounts of methanol. When acetone (30 ml) was added to a solution of *N-oxide* (0.4 g) in hot methanol (15 ml) it separated in long prisms, m.p. 201 °C (decomp.) (Found: C, 55.6; H, 7.6; N, 8.1%. Calc. for  $C_8H_{13}O_3N$ : C, 56.1; H, 7.7; N, 8.2%).

(h) *Paper Chromatography*.—Paper chromatograms were run on Whatman No. 1 paper with ascending solvent flow in cabinets of all-glass interior and large enough to take 22 by 18 in. sheets. The butanol-acetic acid solvent was the upper phase resulting from shaking butanol with an equal volume of aqueous acetic acid (5%); the butanol-ammonia was a homogeneous mixture of butanol (30 parts), water (5 parts), and 880 ammonia (1 part). Minor variations in these solvents caused little change in  $R_F$  values. After completion of a run, papers were air dried and placed for several minutes in a glass tank containing iodine crystals and vapour. The  $R_F$  values recorded in Table 2 are those obtained in a room kept at  $17 \pm 1^\circ\text{C}$ , using equilibration and development periods of approx. 3 and 16 hr, respectively. For general purposes the tanks were used in the main laboratory which was subject to wide temperature variations and the papers were developed without an equilibration period. Under these conditions, the  $R_F$  values fluctuated widely with seasonal and daily atmospheric changes, tending to be higher in summer than in winter; for example, the  $R_F$  of heliotrine in butanol-acetic acid varied from 0.41 to 0.55. Since the  $R_F$  values of the other heliotrope bases varied similarly, this caused little inconvenience if standard heliotrine and lasiocarpine spots were applied to each paper.

(i) *Partition Chromatography and Estimation of the Alkaloids*.—For assay purposes kieselguhr ("Hyflo-Super-Cel"; 20 g), previously moistened with potassium phosphate buffer solution (8 ml) of pH 8.0,  $d\ 1.1$ , was packed into a glass column, c. 1.2 by 30 cm, by slurring in light petroleum and tamping with a close-fitting, perforated plunger. The crude alkaloid ( $2.5$  to  $3.0 \times 10^{-4}$  equiv.) was applied in either of two ways: (i) by dissolving in sulphuric acid (0.4N; 1 ml), treating with sodium hydroxide (1N; 0.6 ml), mixing the resulting solution with kieselguhr (2.5 g), and packing on top of the column, or (ii) by dissolving in chloroform (1 ml), spreading this solution on glass powder, evaporating the chloroform *in vacuo*, and packing the glass powder above the "Hyflo" column. Light petroleum-20% carbon tetrachloride (60 ml), light petroleum-80% carbon tetrachloride (60 ml), carbon tetrachloride (60 ml), carbon tetrachloride-40% chloroform (75 ml), and chloroform (150 ml) were then run through in this order. The eluate was collected in 5 ml fractions, using an automatic collector based on the design of Grant and Stitch (1951). The fractions were titrated directly with *p*-toluenesulphonic acid (0.01N) in chloroform using dimethyl yellow as indicator under which conditions *N-oxides* titrate as strong bases. For eluates containing less than 40% chloroform, it was necessary to add 2 ml chloroform to each fraction before titrating in order to obtain a clearly visible end-point. Plotting the titres against fraction number gave elution curves as illustrated in Figures 1 and 2. In recovering the alkaloids from the combined fractions of each peak, the titrated solutions were shaken with dilute alkali, and the organic layer separated and combined with an additional chloroform extract of the alkaline liquor. The organic solvent was removed and the residue

taken up in sufficient methanol to give a solution of suitable concentration for paper chromatography (a volume of methanol equal to one-sixth of the total acid titre for the peak). The  $R_f$  values of the peak alkaloids were then determined (the dimethyl yellow present caused no interference since in butanol-acetic acid, it travels close to the solvent front).

For assay, the crude alkaloid was prepared from a methanol extract of not less than 100 g of the milled plant. The extract was evaporated, the residue extracted with HCl (2%), and the solution divided into two equal parts, one of which was reduced with zinc dust with sufficient sulphuric acid to make the acid strength 2N. Both parts were then basified with ammonia and extracted with chloroform to give "unreduced" and "reduced" alkaloids. These were made up to appropriate known volumes in methanol and aliquots titrated (after evaporation). An aliquot of the solution containing approx.  $2.5$  to  $3 \times 10^{-4}$  equiv. of base was then applied to the column as described above.

#### IV. ACKNOWLEDGMENTS

The authors are indebted to Mr. P. M. Hunter and Mr. M. Linton for carrying out large-scale extractions; to Dr. L. B. Bull and Mr. A. T. Dick for assistance in the collection of plant material; and to Professor A. Camara, Estacao Agronomica Nacional, Portugal, and Mr. W. Hartley for a specimen of *H. europaeum* from Portugal.

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## THE ALKALOIDS OF *HELIOTROPIMUM EUROPAEUM* L.

### II. ISOLATION AND STRUCTURES OF THE THIRD MAJOR ALKALOID AND TWO MINOR ALKALOIDS, AND ISOLATION OF THE PRINCIPAL N-OXIDES

By C. C. J. CULVENOR\*

[Manuscript received April 9, 1954]

#### Summary

The third major alkaloid of *Heliotropium europaeum* L. is isolated and shown to be heliotridine esterified on the methylol hydroxyl with lasiocarpic acid (2,3-dihydroxy-4-methoxy-2-methylpentane-3-carboxylic acid). Two minor alkaloids isolated are shown to be supinine (supinidine esterified with trachelanthic acid) and supinidine esterified with heliotric acid (3-hydroxy-4-methoxy-2-methylpentane-3-carboxylic acid). The N-oxides of heliotrine, lasiocarpine, and the third major base have been isolated from the seed of *H. europaeum*.

#### I. INTRODUCTION

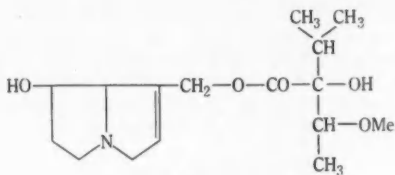
In Part I of this series (Culvenor, Drummond, and Price 1954), the two principal crystalline bases of *Heliotropium europaeum* L. were identified as heliotrine (I) and lasiocarpine (II), and it was shown that at least three other bases, one of which was a major component, were present. The three unidentified bases have now been isolated and their structures have been determined. The N-oxides of the three major alkaloids have also been obtained directly from plant extracts.

Isolated in the first instance by partition chromatography under conditions similar to those of the analytical separation described in Part I, the new bases are those corresponding to the C, F, and G peaks of the elution curve, and they are referred to in the sequel by these letters. Their empirical formulae and physical constants are given in Table 1.

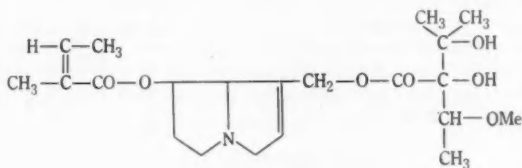
Because of the comparatively low capacity of the partition columns, other methods of separation were required for large amounts of alkaloid. Use was made of the fact that trichloroethylene extracts only lasiocarpine, heliotrine, and base C from a basified aqueous extract, while subsequent extraction with butanol yields bases F and G with some heliotrine. The mixture of lasiocarpine, heliotrine, and base C was separated into concentrates of the component bases by extraction from aqueous solution at increasing pH levels, and the mixture of heliotrine and bases F and G was resolved by counter-current distribution between aqueous sodium bicarbonate and a mixture of chloroform and carbon tetrachloride.

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Base *G* was obtained as a water-soluble gum or glass, and its *N*-oxide,  $C_{16}H_{27}O_7N$ , was the only crystalline derivative prepared. Some *N*-oxides retain tenaciously water or other solvent molecules (cf. lasiocarpine *N*-oxide, Part I), but this oxide proved not to be solvated since degradative results



(II)



(III)

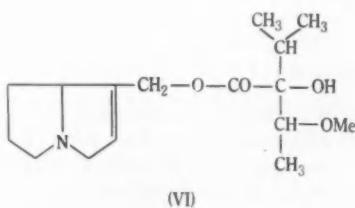
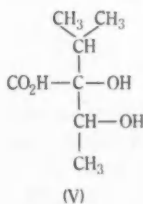
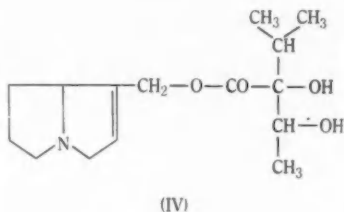
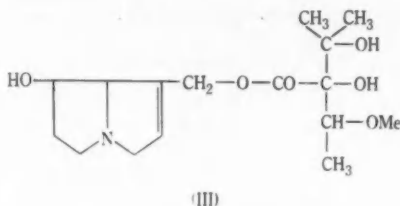
confirmed the formula of the free base as  $C_{16}H_{27}O_6N$ . Hydrolysis of the free base gave heliotridine and a liquid acidic product which gave two spots at  $R_F$  0.25 and 0.11 on a paper chromatogram run in butanol-ammonia. Lasiocarpic acid has  $R_F$  0.25 in this solvent and hydrolysis of lasiocarpine gave rise to an

TABLE I  
EMPIRICAL FORMULAE AND PHYSICAL CONSTANTS OF THE ALKALOIDS OF  
H. EUROPAEUM

Base	Empirical Formula	Melting Point (°C)	Specific Rotation, $[\alpha]_D$
<i>C</i>	$C_{16}H_{27}O_4N$	67–68	–12.0° (c, 5, ethanol)
<i>F</i>	$C_{15}H_{25}O_4N$	148–149	–11.5° (c, 4.9, ethanol)
			–12.1° (c, 2.0, ethanol)
<i>G</i>	$C_{16}H_{27}O_6N$	—	+10.9° (c, 2.47, ethanol)

acidic product showing (after removal of angelic acid) the same two spots in similar proportions. It is very likely, therefore, that the acids resulting from the hydrolysis of base *G* were lasiocarpic acid and its alkaline decomposition product (see Part I). Attempts to isolate the acids as their phenacyl or *p*-phenyl-phenacyl esters failed to give crystalline products.

In the presence of palladized charcoal, the *N*-oxide of base *G* took up 3 moles of hydrogen to give lasiocarpic acid and a base,  $C_8H_{15}ON$ ,  $[\alpha]_D^{17} -2.5^\circ$  (*c*, 4.8 in water). This base gave a picrate identified by mixed melting point with that of hydroxyheliotridane from lasiocarpine or heliotrine and was clearly a mixture of the two possible isomers resulting from saturation of the nuclear double bond present in heliotridine. Base *G* is therefore an allyl ester and has the structure III; that is, it is heliotridine esterified on the methylol hydroxyl with lasiocarpic acid (2,3-dihydroxy-4-methoxy-2-methylpentane-3-carboxylic acid).



Base *F* is isomeric with supinine (IV), an alkaloid isolated by Menshikov and Gurevich (1949) from *H. supinum*, and with the exception of the specific rotation, the physical properties of the two compounds are similar (the available data are compared in Table 2). Alkaline hydrolysis of supinine was reported to give supinidine and racemic trachelanthic acid (i.e. of zero rotation), and from the properties recorded in Table 2 the base derived similarly from alkaloid *F* is clearly identical with supinidine. The acid obtained by hydrolysis of base *F* possessed a definite positive rotation but there is no doubt that it is

identical with trachelanthic acid. All possible stereoisomeric forms of 2,3-dihydroxy-4-methylpentane-3-carboxylic acid (V) have been synthesized by Adams and van Duuren (1952) and by Dry and Warren (1952), and both pairs of workers have identified the (+)-*threo*- [or (+)-*cis*-] form with the acid which occurs esterified in trachelanthine and supinine. The acid from base *F* agreed fairly closely in its properties with this synthetic compound and its identity was confirmed by direct comparison with the acid obtained by demethylation of heliotric acid, which was stated by Adams and van Duuren (1953) to be identical with the (+)-*cis*- isomer of V. Despite the differences in the reported specific rotations, base *F* must be identical with supinine.

TABLE 2  
COMPARISON OF BASE *F* WITH SUPININE

Details	Base <i>F</i>	Supinine
Alkaloid .. ..	$C_{15}H_{25}O_4N$	$C_{15}H_{25}O_4N$
Melting point (°C) ..	148-149	146-147.5
[ $\alpha$ ] <sub>D</sub> (ethanol) .. ..	-11.5° (c, 4.88) -12.1° (c, 1.98)	-23.8°
Hydrolysis base .. ..	$C_8H_{13}ON$	$C_8H_{13}ON$
[ $\alpha$ ] <sub>D</sub> (ethanol) .. ..	-10.3° (c, 1.65)	-9.45°
Picrate (m.p. °C) .. ..	144	142-143
Product with Ni/H <sub>2</sub> .. ..	$C_8H_{15}ON$	<i>iso</i> Retronecanol, $C_8H_{15}ON$
[ $\alpha$ ] <sub>D</sub> (ethanol) .. ..	-75° (c, 1.01)	-78.2°
Picrate (m.p. °C) .. ..	193-194	193-194
Hydrolysis acid .. ..	$C_7H_{14}O_4$	"Racemic" trachelanthic acid,* $C_7H_{14}O_4$
Melting point (°C) ..	93-94	
[ $\alpha$ ] <sub>D</sub> (ethanol) .. ..	+2.3° (c, 1.7)	(0°)
Brucine salt (m.p. °C) ..	230	—

\* For (+)-*threo*-2,3-dihydroxy-4-methylpentane-3-carboxylic acid, Dry and Warren (1952) give m.p. 92 °C, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +2.2° (c, 1 in ethanol), brucine salt, m.p. 225 °C. Adams and van Duuren (1952) give m.p. 89 °C, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +2.9° (c, 2.5 in water), brucine salt, m.p. 217-220 °C.

The descriptions in the literature of the preparation of trachelanthic acid by hydrolysis of trachelanthine and supinine, led Adams and van Duuren (1952) to regard these products as partially racemized, and in support of this belief, they described the conversion of the (+)-*cis*- isomer of V into the (±)-*cis*-racemate by heating in aqueous alcoholic alkali. The acid from hydrolysis of base *F*, however, showed no sign of being partially racemized and contrary to the report of Adams and van Duuren, it is now found that the (+)-*cis*- acid is unchanged in melting point and specific rotation under the conditions used by these authors or under more vigorous conditions (refluxing with sodium hydroxide in amyl alcohol). Thus true racemization of trachelanthic acid (i.e. conversion into one racemate), as envisaged by Adams and van Duuren, does not occur under the usual conditions of hydrolysis and it is probable that both trachelanthic acid and its stereoisomer, viridifloric acid, are optically pure compounds. A

possible explanation of reported cases of trachelanthic acid lacking optical activity may be found in the low specific rotation, coupled with a decrease in the rotation of trachelanthic acid in aqueous solution as the concentration is increased (Fig. 1).

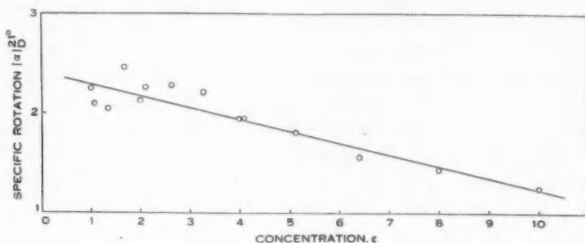


Fig. 1.—Specific rotation of (+)-*threo*-2,3-dihydroxy-4-methylpentane-3-carboxylic acid in water.

Hydrolysis of alkaloid *C* gave a base,  $C_8H_{13}ON$ , whose properties and derivatives were identical with those of supinidine from base *F*, and an acid,  $C_8H_{16}O_4$ , identified by direct comparison with heliotric acid. Thus alkaloid *C* has structure VI and is supinidine esterified with heliotric acid (3-hydroxy-4-methoxy-2-methylpentane-3-carboxylic acid).

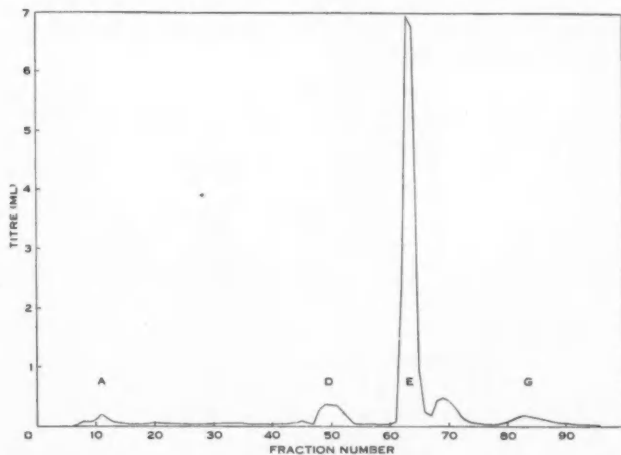


Fig. 2.—“Unreduced” alkaloid of the seed of *H. europaeum* chromatographed on kieselguhr-pH 8.0 buffer.

A base,  $C_{12}H_{17}O_4N$  or  $C_{12}H_{19}O_4N$ , not detected in alkaloid from whole plant, was isolated from a large-scale extraction of heliotrope seed. The amount obtained was too small to permit of structural determination but the compound is probably an *N*-oxide, since it gives a red-brown colour with acetic anhydride,

is changed on reaction with zinc and sulphuric acid, and has the solubilities expected for an *N*-oxide. Pyrrolizidine alkaloids with so few carbon atoms have not previously been isolated, although Menshikov, Denisova, and Massagetov (1952) recently obtained a base,  $C_{13}H_{21}O_3N$ , from *Turneforcica* (*Tournefortia*?) *sibirica*.

Heliotrope seed was used as the starting point for isolation of the *N*-oxides because of the high proportion of alkaloids in the *N*-oxide form (cf. Part I). In this case, the crude alkaloid isolated with chloroform was shown by assay to consist largely of lasiocarpine *N*-oxide (Fig. 2). A small amount of this *N*-oxide was obtained by direct crystallization from acetone but the bulk of it was isolated by partition chromatography. The other *N*-oxides were extracted from the residual aqueous solution with butanol and purified by chromatography on alumina. The identities of all three *N*-oxides were confirmed by direct comparisons and by reduction to the parent alkaloids.

## II. EXPERIMENTAL

All melting points are corrected. Microanalyses were carried out in the C.S.I.R.O. Micro-analytical Laboratory.

(a) *Isolation of Bases C, F, and G from Heliotrope Seed.*—Ground heliotrope seed (70 lb) was extracted with hot methanol and the extract concentrated to a volume of 10 gal. This solution was washed twice with 10 gal portions of light petroleum, and the washings, which contained no basic material, were discarded. The methanol phase was evaporated and the residue extracted with dilute sulphuric acid. The acid extract was made approximately 2N with respect to sulphuric acid, stirred with excess zinc dust for 8 hr, filtered, and made alkaline to phenolphthalein with ammonia. This solution was extracted three times with trichloroethylene and then three times with butanol.

TABLE 3  
EXTRACTION AND  $R_F$  VALUES OF THE ALKALOID FRACTIONS

Fraction	pH	Solvent (ml)	Product (g)	$R_F$ Values*
1	5.0	$C_6H_6$ , 2 × 500	10.0	0.67
2	7.0	$CHCl_3$ , 3 × 300	78.3	0.67, 0.55
3	7.5	$CHCl_3$ , 3 × 300	23.0	0.56, 0.47
4	8.5	$CHCl_3$ , 3 × 300	31.8	0.47
5	10.0	$CHCl_3$ , 6 × 300	1.71	0.47, 0.41, 0.31
Heliotrine, lasiocarpine				0.47, 0.66

\* Underlining indicates spot present in major amount.

(i) *Trichloroethylene Extract.* The residue on evaporation was dissolved in dilute phosphoric acid (1.5 l.) and re-extracted at increasing pH levels. Details of the extraction and  $R_F$  values of the alkaloid fractions obtained are given in Table 3 (the pH shown is that of the aqueous phase after shaking with the organic phase). Fraction 1 contained a little lasiocarpine but being mostly non-basic material was discarded. Fraction 5 was later added to other concentrates of base *F*. Fraction 4 was crystallized from acetone and gave heliotrine (19.2 g), m.p. 123–125 °C. Fraction 2 was dissolved in a 4 : 1 mixture of carbon tetrachloride and chloroform (3 l.) and passed through a column packed with kieselguhr and pH 4 buffer (150 ml), development with the same

solvent being continued until no more alkaloid was eluted. The eluate yielded lasiocarpine (62 g), m.p. 93–94 °C, while crude alkaloid which was largely base *C* was recovered from the column packing by extracting with water, making the solution alkaline, and extracting with chloroform. This base and fraction 3 were combined and extracted several times with hot light petroleum (b.p. 50–60 °C). The residue was heliotrine (11.2 g), m.p. 124–125 °C, and the light petroleum extract when concentrated, seeded with base *C*, and cooled in ice gave crude base *C* as a cream coloured solid (7.0 g), m.p. 55–60 °C.

Successive recrystallization of base *C* from a small amount of light petroleum, aqueous acetone, and light petroleum produced large transparent prisms, m.p. 67–68 °C,  $[\alpha]_D^{15} -12.0^\circ$  (c, 5.15 in ethanol) (Found: C, 64.8; H, 9.2; N, 4.8; OMe, 10.2%; equiv. wt. 302. Calc. for  $C_{16}H_{27}O_4N$ : C, 64.6; H, 9.2; N, 4.7; 1 OMe, 10.4%; equiv. wt. 297). Base *C* is soluble in both light petroleum and water and is very soluble in all other solvents. Unless pure, it colours reddish brown within a few days; passage through alumina, from which it is eluted by benzene, removes most of the colour but the product rapidly discolours again.

TABLE 4  
EMERGENT FRACTIONS COMBINED ACCORDING TO  $R_F$  VALUES

Fraction	$R_F$ Values*	Residue on Evaporation (g)
Emergent 1-6 .. ..	0.62, 0.53, 0.44	5.66
" 7-12 .. ..	0.54, 0.44	37.0
" 13-18 .. ..	0.48	11.8
" 19-24 .. ..	0.46	5.96
Tube 24 .. ..	0.46	(22-24): 1.78
" 22 .. ..	0.44	
" 20 .. ..	0.42	
" 18 .. ..	0.42	(17-21): 1.14
" 16 .. ..	0.39	
" 14 .. ..	0.40	(10-16): 1.00
" 12 .. ..	0.39	
" 10 .. ..	0.40	
" 8 .. ..	0.26	
" 6 .. ..	0.26	(1-9): 2.20
" 4 .. ..	0.26	
" 2 .. ..	0.26	

\* Underlining indicates spot present in major amount.

(ii) *Butanol Extract.* After removal of the solvent under reduced pressure, the residue was extracted with dilute hydrochloric acid (2 l.), and the solution made alkaline to phenolphthalein and extracted thoroughly with chloroform (10 × 1.5 l.). The first four extracts yielded a gum (118.5 g),  $R_F$  0.26, 0.43; the next six, a gum (8.8 g),  $R_F$  0.26. The product from the latter group of extracts was oxidized with hydrogen peroxide by the method described below and gave the *N*-oxide of base *G* (2.4 g), m.p. 167–168 °C. The gum from the first extracts was subjected to a counter-current distribution using saturated aqueous sodium bicarbonate (90 ml) as stationary phase and a 1:1 mixture of chloroform and carbon tetrachloride (60 ml) as mobile phase. The first 4 transfers were carried out in separating funnels to allow adjustment of volumes and filtering from precipitated non-basic material, and subsequent operations in a 25-plate distributing machine of the type described by Lathe and Ruthven (1951). After 30 transfers, the incoming mobile phase was changed to 4:1 chloroform-carbon tetrachloride and 18 more transfers made. The emergent fractions of mobile phase were combined in sets of 6, and the mobile phases in the tubes were removed and combined according to  $R_F$  values as shown in Table 4. The aqueous

phases were grouped in the same way as the mobile phases and the alkaloid present recovered with chloroform. The products and their  $R_F$  values are shown in Table 5.

The products from mobile phases 1 to 9 and aqueous phases 1 to 10 were combined and passed through alumina in 9:1 chloroform-ethanol. The eluate was evaporated (some loss by accident) and the residue converted into the *N*-oxide by keeping in ethanol (20 ml) and hydrogen peroxide (30%; 20 ml) for 2 days, removing unchanged peroxide with manganese dioxide, filtering, washing the filtrate with chloroform, and evaporating the aqueous solution to dryness *in vacuo*. Recrystallization from acetone-methanol gave the *N*-oxide of base G (12.0 g) as colourless needles, m.p. 171 °C (decomp.),  $[\alpha]_D^{17} + 25.3^\circ$  (c, 2.77 in ethanol) (Found: C, 55.8; H, 7.8; N, 3.9%; equiv. wt. 348. Calc. for  $C_{16}H_{27}O_7N$ : C, 55.6; H, 7.9; N, 4.05%; equiv. wt. 345). The equiv. wt. was determined by titration in chloroform with *p*-toluenesulphonic acid. The *N*-oxide was reduced with zinc dust and sulphuric acid (2N) to give base G as a colourless gum,  $[\alpha]_D^{17} + 10.9^\circ$  (c, 2.47 in ethanol). It was kept in a refrigerator.

Crystallization of the products from mobile phases 10 to 16 and aqueous phases 11 to 17 from acetone gave base F (1.83 g) as colourless prisms, m.p. 146–148 °C. After two recrystallizations from acetone, it formed large prisms, m.p. 148–149 °C,  $[\alpha]_D^{17} - 11.5^\circ$  (c, 4.88 in ethanol; solution supersaturated),  $-12.1^\circ$  (c, 1.98 in ethanol) (Found: C, 63.9; H, 8.9; N, 5.1%; equiv. wt. 283. Calc. for  $C_{15}H_{25}O_4N$ : C, 63.6; H, 8.9; N, 4.9%; equiv. wt. 283).

TABLE 5  
AQUEOUS PHASES AND THEIR  $R_F$  VALUES

Fraction	Base Content (g)	$R_F$ Values*
Aqueous phase 1–10	41.8	0.28, 0.45, 0.72
“ “ 11–17	3.6	0.28, 0.40, 0.47
“ “ 18–22	0.8	0.42
	(after recrystallization)	
“ “ 23–25	1.31	0.42

\* Underlining indicates spot present in major amount.

(b) *Base*  $C_{12}H_{17}O_4N$  or  $C_{12}H_{19}O_4N$ .—The product from emergent fractions 7 to 12, crystallized from acetone, gave heliotrine (15.9 g), m.p. 122–124 °C, together with another compound (1.6 g), m.p. 145–147 °C,  $R_F$  0.49, which was in the form of spherulites and readily separated by hand-picking. The spherulites would not redissolve in hot acetone but on recrystallization from acetone-methanol formed colourless prisms, m.p. 158–159 °C (decomp.) (Found: C, 59.8; H, 7.6; N, 5.8%. Calc. for  $C_{12}H_{17}O_4N$ : C, 60.2; H, 7.2; N, 5.9%. Calc. for  $C_{12}H_{19}O_4N$ : C, 59.7; H, 7.9; N, 5.8%). Reduction with zinc and sulphuric acid gave a product which separated from acetone as an oil mixed with needles, m.p. 118–121 °C. When heated with charcoal in acetone-methanol, the base decomposed into acetone soluble material.

(c) *Partition Chromatography*.—The methods and solvents were as described in Part I. Although the separations were not as complete as in the assay columns, about 10 g crude bases could be resolved well enough for preparative purposes on a column 5.0 by 90 cm, holding 400 g kieselguhr and 200 ml buffer solution. The eluate was collected in 50 ml fractions of which 1 ml aliquots were titrated with *p*-toluenesulphonic acid (0.01N) in chloroform to determine the position of elution of the bases.

(d) *Hydrolysis of Base G*.—Base G (0.45 g) from reduction of purified *N*-oxide, was heated for 2 hr at 100 °C with aqueous barium hydroxide, after which the solution was treated with excess carbon dioxide, filtered, made acid to Congo red with hydrochloric acid, and continuously extracted with chloroform. The first 8 hr extraction gave a brown gum (0.13 g) and the next 8 hr yielded a colourless gum (0.01 g). Paper chromatograms on these acidic products, made



with butanol-ammonia solvent (see Part I), gave spots of  $R_F$  0.25, 0.11, for the main fraction and  $R_F$  0.11 only for the second fraction. Lasiocarpic acid under these conditions had  $R_F$  0.25. Hydrolysis of lasiocarpine was found to give acidic products, which after removal of angelic acid by crystallization from water, showed spots of the same  $R_F$  values, 0.25, 0.11. Attempts to obtain a pure acid from the hydrolysis products of base *G* by way of the phenacyl or *p*-phenylphenacyl esters, were unsuccessful. After removing acidic material, the hydrolysis products were made very strongly alkaline and again extracted continuously with chloroform to give a gum (0.16 g) which crystallized spontaneously. Distillation of this material at 140–170 °C/0.5 mm produced a yellow solid (some resinification) which crystallized from acetone in colourless needles, m.p. 116–117 °C, mixed m.p. with heliotridine, 117–118 °C (Found: C, 62.1; H, 8.4; N, 9.1%. Calc. for  $C_8H_{13}O_2N$ : C, 62.0; H, 8.4; N, 9.0%).

(e) *Hydrogenation of the N-Oxide of Base G*.—On shaking in dilute hydrochloric acid with hydrogen and palladized charcoal (0.1 g), the *N*-oxide (1.32 g) absorbed 225 ml hydrogen rapidly and an additional 56 ml slowly. Theoretical uptake: 220 ml for 3 moles, or 292 ml for 4 moles. The solution was filtered and continuously extracted with methylene chloride (4 hr) to give lasiocarpic acid (0.7 g), forming needles from benzene-light petroleum, m.p. 96–97 °C, mixed m.p. 96–97 °C,  $[\alpha]_D^{17} +10.0^\circ$  (c, 5.44 in ethanol) (Found: C, 50.4; H, 8.5%. Calc. for  $C_8H_{16}O_3$ : C, 50.0; H, 8.4%). The residual aqueous solution was made alkaline with potassium carbonate and continuously extracted with chloroform. The product (0.54 g) had similar  $R_F$  values to hydroxyheliotridane (0.33 in butanol-acetic acid; 0.76 in butanol-ammonia). It was twice distilled from a bulb tube at 140 °C/13 mm, taking precautions to exclude carbon dioxide and moisture from the distillate until samples had been removed for analysis and m.p. determinations. The base crystallized readily, the upper point of its m.p. range being 38 °C, the upper point for a mixture with hydroxyheliotridane from heliotrine was 43 °C. The specific rotation was  $[\alpha]_D^{17} -2.5^\circ$  (c, 4.8 in water) (Found: C, 67.5; H, 10.6; N, 10.1%. Calc. for  $C_8H_{15}ON$ : C, 68.0; H, 10.7; N, 9.9%). The base picrate separated from ethanol in yellow needles, m.p. 192 °C (decomp.) (Found: C, 45.6; H, 5.0; N, 15.0%. Calc. for  $C_{14}H_{19}O_8N_4$ : C, 45.4; H, 4.9; N, 15.1%). The methiodide formed prisms from acetone, m.p. 288 °C (uncorr., copper block) (Found: C, 38.5; H, 6.3; N, 5.0%. Calc. for  $C_9H_{18}ONI$ : C, 38.1; H, 6.4; N, 4.9%).

(f) *Hydrolysis of Base F*.—The base (0.6 g) was heated at 100 °C for 2 hr with sodium hydroxide (2.5N; 15 ml) and the acidic and basic products isolated with chloroform as in the hydrolysis of base *G*. The resulting acid (0.39 g) crystallized from benzene-light petroleum in small pink rosettes, m.p. 93–94 °C. Sublimation at 100 °C/0.02 mm removed the colour and a further crystallization gave colourless rosettes, m.p. 93–94 °C,  $[\alpha]_D^{18} +2.3^\circ$  (c, 1.7 in ethanol) (Found: C, 51.8; H, 8.5%. Calc. for  $C_7H_{14}O_4$ : C, 51.8; H, 8.7%). The brucine salt of the acid separated from ethanol in small prisms, m.p. 230 °C (Found: C, 65.0; H, 7.2; N, 5.0%. Calc. for  $C_{20}H_{40}O_8N_2$ : C, 64.7; H, 7.2; N, 5.0%). The liquid base from the hydrolysis (0.29 g), after two distillations at 90–95 °C/0.1 mm had  $[\alpha]_D^{18} -10.3^\circ$  (c, 1.65 in ethanol) (Found: C, 69.3; H, 9.2; N, 10.4%. Calc. for  $C_8H_{13}ON$ : C, 69.1; H, 9.4; N, 10.1%). The picrate formed needles from ethanol, m.p. 144 °C (*in vacuo*) (Found: C, 45.7; H, 4.3; N, 15.0%. Calc. for  $C_{14}H_{18}O_8N_4$ : C, 45.6; H, 4.4; N, 15.2%). On shaking with hydrogen and fresh Raney nickel at room temperature and pressure, the base (0.166 g) absorbed 1 mole of hydrogen (Found: 27.0 ml; theory: 28.6 ml). The catalyst was filtered off and the product distilled at 80–85 °C/0.1 mm to give a colourless oil,  $[\alpha]_D^{18} -75^\circ$  (c, 1.01 in ethanol) (Found: C, 68.3; H, 10.6; N, 10.2%. Calc. for  $C_8H_{13}ON$ : C, 68.1; H, 10.7; N, 9.0%). The picrate of the reduced base crystallized from ethanol in needles, m.p. 193–194 °C (Found: C, 45.7; H, 5.1; N, 14.8%. Calc. for  $C_{14}H_{18}O_8N_4$ : C, 45.4; H, 4.9; N, 15.1%).

(g) (+)-threo-2,3-Dihydroxy-4-methylpentane-3-carboxylic Acid.—The acid prepared (86% yield) according to Adams and van Duuren (1953) by refluxing heliotric acid with hydrobromic acid (48%), formed prisms from benzene-light petroleum, m.p. 93–94 °C, undepressed on admixture with the acid obtained by hydrolysis of base *F*. Specific rotations of aqueous solutions of varying concentration are given in Figure 1; in ethanol (c, 1.93),  $[\alpha]_D^{21} +3.7^\circ$ . All measurements were made in a 4 decimetre tube.

In different experiments, the acid (1 g) was refluxed (a) for 1.5 hr with sodium hydroxide (10%) in 1 : 1 aqueous ethanol (60 ml), (b) for 8 hr in a similar medium, and (c) for 9 hr in aqueous sodium hydroxide (30% ; 30 ml). In each case, it was recovered completely and on crystallizing from benzene-light petroleum, had m.p. and mixed m.p. 93–94 °C,  $[\alpha]_D^{21} + 2.1^\circ$  (c, 2.5 in water). The acid (1 g) was also refluxed for 7 hr with sodium hydroxide (10%) in amyl alcohol (60 ml), the solution cooled and extracted with water (5 × 20 ml), and the aqueous extract acidified and extracted with chloroform to give unchanged acid (1.0 g) which after crystallization from benzene-light petroleum had m.p. and mixed m.p. 93–93.5 °C,  $[\alpha]_D^{20} + 2.4^\circ$  (c, 0.73 in water). In none of these experiments was a volatile carbonyl compound detected.

(h) *Hydrolysis of Base C*.—After heating base C (1.0 g) at 100 °C for 2 hr with sodium hydroxide (2.5N ; 20 ml) and ethanol (5 ml), the ethanol was removed by distillation, and the solution made acid to Congo red with hydrochloric acid and continuously extracted with methylene chloride to give heliotric acid (0.63 g). After boiling in light petroleum with charcoal to remove a red contaminant, and sublimation at 100 °C/15 mm the acid had m.p. 92–93 °C mixed m.p. 92–93 °C,  $[\alpha]_D^{16} - 9.8^\circ$  (c, 4.9 in water) (Found : C, 54.7 ; H, 9.0%. Calc. for  $C_8H_{16}O_4$  : C, 54.5 ; H, 9.2%). The hydrolysis solution was made strongly alkaline and extracted with chloroform to give a base (0.49 g) which after two distillations at 100–105 °C/0.3 mm had  $[\alpha]_D^{17} - 10.3^\circ$  (c, 1.95 in ethanol) (Found : C, 69.0 ; H, 9.5 ; N, 10.3%. Calc. for  $C_8H_{13}ON$  : C, 69.0 ; H, 9.4 ; N, 10.1%). The picrate formed needles from ethanol, m.p. 144 °C (*in vacuo*), alone or on admixture with supinidine picrate from base F (Found : C, 45.8 ; H, 4.4 ; N, 15.0%. Calc. for  $C_{14}H_{16}O_8N_4$  : C, 45.6 ; H, 4.4 ; N, 15.2%). Reduction of the base with hydrogen and Raney nickel gave an oil whose picrate crystallized from ethanol in needles, m.p. 193–194 °C ; mixed m.p. with isoretronecanol picrate derived from base F, 193–194 °C (Found : C, 45.8 ; H, 4.7 ; N, 15.0%. Calc. for  $C_{14}H_{18}O_8N_4$  : C, 45.4 ; H, 4.9 ; N, 15.1%).

(i) *Isolation of Lasiocarpine and Heliotrine N-Oxides*.—A methanol extract of heliotrope seed (172 g) was concentrated and washed with light petroleum to remove fats. The methanol was then removed completely and the residue extracted with dilute hydrochloric acid. The acid extract was made alkaline and extracted with chloroform to give fraction 1 (0.70 g). Further extraction with butanol, evaporation of the butanol extracts *in vacuo*, and extraction of the residue with ethanol gave fraction 2 (3.2 g). Fraction 1 was dissolved in hot acetone and on cooling and seeding with lasiocarpine N-oxide, deposited this substance (60 mg) as colourless prisms, m.p. 129–130 °C (decomp.), undepressed by admixture with synthetic lasiocarpine N-oxide. Recrystallization from acetone gave needles, m.p. 133 °C (decomp.) (Found : C, 56.9 ; H, 7.9 ; N, 3.4%. Calc. for  $C_{21}H_{33}O_8N.H_2O$  : C, 56.6 ; H, 7.9 ; N, 3.2%). Reduction of the naturally occurring sample of N-oxide with zinc and sulphuric acid furnished lasiocarpine, m.p. and mixed m.p. 94–95 °C. The mother liquor of fraction 1 was evaporated and the constituents separated on a small partition column (25 g "Hyflo" ; 20 ml pH 7.5 buffer). Evaporation of the appropriate eluate fraction gave a light amber gum (0.19 g) which from ethyl acetate formed needles (0.14 g), m.p. 127–128 °C, undepressed on admixture with lasiocarpine N-oxide. Reduction of this sample also produced lasiocarpine, m.p. and mixed m.p. 95–96 °C.

The crude fraction 2 was extracted with chloroform and the extracts passed into a column of alumina. A further 200 ml chloroform and 200 ml chloroform (95%)–ethanol (5%) were passed through the column without eluting any appreciable amount of material. Elution with 9 : 1 chloroform–ethanol (1000 ml) and 4 : 1 chloroform–ethanol (900 ml) produced white solids (0.41 g and 0.34 g respectively) both crystallizing from methanol–acetone in needles, m.p. 169.5–170.5 °C, undepressed by admixture with heliotrine N-oxide (Found : C, 58.7 ; H, 8.3 ; N, 4.1%. Calc. for  $C_{16}H_{27}O_6N$  : C, 58.4 ; H, 8.2 ; N, 4.3%). Reduction with zinc and sulphuric acid gave heliotrine, m.p. 124–125 °C, mixed m.p. 125–126 °C.

(j) *Isolation of the N-Oxide of Base G*.—An aqueous acid extract of total bases from heliotrope seed (2.5 kg) was obtained in the usual way, and reduced with zinc and sulphuric acid (intermittent shaking for 4 hr and then keeping overnight ; incompleteness of the reduction was not intentional). The mixture was filtered, made alkaline with excess ammonia, and extracted with trichloroethylene and then with butanol. The butanol extract was evaporated to dryness

and extracted with ethanol. The ethanol extract was re-evaporated and the residue extracted with chloroform-5% ethanol and with hot chloroform. The extracts were applied to an alumina column (2.9 by 44 cm), developed with chloroform, and then eluted with 9 : 1 chloroform-ethanol (1200 ml; giving a concentrate of base *G*, 5.50 g) and 4 : 1 chloroform-ethanol (1200 ml, eluate 2; and 1000 ml eluate 3). Crystals separated from the gum (0.42 g) obtained from eluate 3; the mixture was boiled with acetone (50 ml) and filtered. Concentration of the filtrate to half-volume, cooling and seeding with base *G* *N*-oxide, produced this substance (0.2 g) as colourless needles, m.p. 170 °C (decomp.), mixed m.p. 169–170 °C,  $R_F$  (butanol-acetic acid) 0.36 (Found: C, 55.9; H, 8.0; N, 2.8%. Calc. for  $C_{16}H_{17}O_2N$ : C, 55.8; H, 7.8; N, 3.9%). When this analysis was performed, only low *N*-figures of about 3% had been obtained for authentic base *G* *N*-oxide. The satisfactory *N*-analysis reported above for this compound was obtained by grinding the sample with the oxidizing agent before combustion. Reduction of the naturally occurring *N*-oxide with zinc and sulphuric acid gave in good yield a colourless gum of  $R_F$  0.28.

### III. ACKNOWLEDGMENTS

The author wishes to thank Mr. P. M. Hunter for carrying out the large-scale extraction of heliotrope seed, and Dr. J. R. Price for his interest and advice.

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# THE SESQUITERPENE ALCOHOL OF *MYOPORUM CRASSIFOLIUM* FORST.

By K. G. O'BRIEN,\* A. R. PENFOLD,† M. D. SUTHERLAND,‡  
and R. L. WERNER§

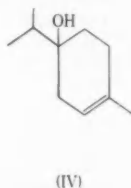
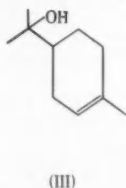
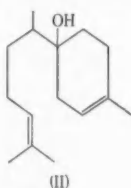
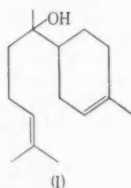
[Manuscript received April 8, 1954]

## Summary

The principal sesquiterpene alcohol (anymol) of the wood oil of *Myoporum crassifolium* Forst. is a stereoisomer of bisabolol. A convenient method of detecting methyl groups attached to the hydroxyl-bearing carbon of tertiary alcohols involves the infrared examination of the pyrolysate of the phenylazophenylurethane for bands due to  $=CH_2$ .

## I. INTRODUCTION

A decision between formulae I and II put forward by O'Brien, Penfold, and Werner (1953) for the principal sesquiterpene alcohol (here called anymol) from the essential oil of the wood of *Myoporum crassifolium* Forst. was prevented by exhaustion of the original supply of oil and the apparent impossibility of



obtaining a further quantity. This difficulty has now been overcome by making use of the only crystalline derivative of anymol that had been obtained, namely, the phenylazophenylurethane, to determine the location of the hydroxyl thus leading to formula I for anymol.

$\alpha$ -Terpineol (III) and terpinen-4-ol (IV) may be regarded as model substances corresponding to the two possibilities (I and II) for the structure of anymol. The phenylazophenylurethanes ("azourethanes") (Davenport and Sutherland 1950) of III and IV decompose with vigorous gas evolution above 170 °C yielding a distillate of terpenes and a residue which is principally aminoazobenzene. This reaction is analogous to the pyrolysis of methyl xanthates (O'Connor and Nace 1952) and may well proceed by a similar mechanism with the resultant advantage of freedom from rearrangements. The advantage of phenylisocyanate as a dehydrating agent in this respect has been noted (Bacon and Farmer 1937).

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An alternative manner of decomposition is exhibited by phenylurethanes derived from phenols (Leuckart 1890; Hoshino, Mukaiyama, and Hoshino 1952) or primary alcohols (Schweitzer 1947). In the compounds under consideration, this reaction, which would lead to the regeneration of the alcohol and phenylazo-phenylisocyanate, occurs to a negligible extent, since the pyrolysate shows very weak absorption in the OH stretching region by infra-red examination.

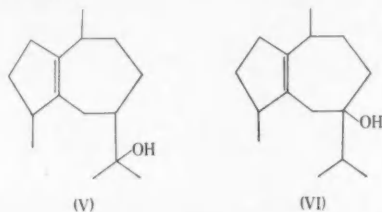


By pyrolysing about 50 mg of azourethane under reduced pressure at 200–210 °C in close proximity to a water cooled finger condenser, a yellow oily condensate is obtained which on cooling deposits crystals of aminoazobenzene but yields sufficient hydrocarbon for infra-red examination. The pyrolysate of the azourethane of III showed bands at 1644 and 887  $\text{cm}^{-1}$ , positions expected for  $\text{R}_2\text{C}=\text{CH}_2$  absorption (for references see O'Brien, Penfold, and Werner 1953). Also observed were bands at 836  $\text{cm}^{-1}$  and another stronger band at 797  $\text{cm}^{-1}$  (Werner and Lark 1954) presumably due to out-of-plane bending of the hydrogen attached to the double bond in the ring. On the other hand, the pyrolysate from the azourethane of IV showed the 1660 and 825  $\text{cm}^{-1}$  bands derived from  $\text{R}_2\text{C}=\text{CRH}$  and no absorption due to the  $\text{R}_2\text{C}=\text{CH}_2$  arrangement. The technique thus appears suitable for discriminating between I and II. The pyrolysate from the azourethane of anymol showed distinct bands at 1640 and 888  $\text{cm}^{-1}$  which indicates clearly the presence of  $\text{R}_2\text{C}=\text{CH}_2$  in the hydrocarbons and establishes the  $\alpha$ -terpineol-like structure I for anymol.

The data recorded in Table 4 of the earlier paper shows that the anyme oil fractionated in an effective type of still yielded six consecutive fractions of the sesquiterpene alcohol of almost constant boiling point, refractive index, density, and optical rotation. It is probable, therefore, that this alcohol is only one of the two diastereoisomers represented by formula I, whereas the bisabolols of Ruzicka and Liguori (1932) and Ruzicka and Capato (1925) must be regarded as mixtures of diastereoisomers which were neither separated nor characterized. Naves has shown the presence of a bisabolol in aqueous layer from neroli oil (Naves 1934) and in cabreuva oil (Naves 1947) by isolating bisabolene trihydrochloride in each case. Similarly Seidel, Müller, and Schinz (1944) have obtained evidence for a bisabolol in French lavender oil. Only in the present instance has an apparently pure compound been isolated and the name anymol is thus appropriate to the particular diastereoisomer isolated from anyme oil and characterized by physical constants and the phenylazophenylurethane of m.p. 103–103.5 °C.

The technique described for detecting the grouping  $\text{CH}_3-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{OH}$  has been applied also to the sesquiterpene alcohol guaial and bands at 1643 and 887  $\text{cm}^{-1}$  were observed in the pyrolysate. This supports V proposed by Plattner and Lemay (1940).

Structure VI, which accommodates more satisfactorily the products of ozonolysis and of chromic acid oxidation (Plattner and Magyar 1942) of crude dihydroguaiane, is excluded.



## II. EXPERIMENTAL

(a) *Pyrolysis*.—Terpinen-4-ol phenylazophenylurethane (50.7 mg) was placed in a side-arm test tube fitted with a water cooled finger condenser reaching to within 1 cm of the sample. The pyrolysis was carried out under a pressure of 100 mm by immersing the bottom of the test tube in an oil-bath at 200–210 °C. Bubbling ceased after about 2 min and the apparatus was then withdrawn from the oil-bath. When the crystallization of the aminoazobenzene on the condenser appeared to be complete, the drop of yellow oil hanging from the tip of the condenser was collected and sealed into a capillary tube. The yield of aminoazobenzene saturated hydrocarbons was 10.5 mg, 57% of the theoretical yield, not allowing for dissolved aminoazobenzene.

$\alpha$ -Terpineol phenylazophenylurethane (87.2 mg) similarly pyrolysed for 4 min yielded 8.5 mg of yellow oil.

Guaial phenylazophenylurethane (56 mg) (G. Lahey and M. D. Sutherland, unpublished data) pyrolysed under 50 mm pressure at 200–220 °C for 5 min gave an oily sludge from which sufficient oil for infra-red examination was obtained by touching with a capillary.

The phenylazophenylurethane (m.p. 100–102 °C; 55 mg) of the sesquiterpene alcohol from *M. crassifolium* similarly treated gave an oily sludge from which the oil could not be drawn off into the capillary. The difficulty was overcome by washing the oil from the sludge with about 2 ml of light petroleum (b.p. <40 °C) into a clean side-arm test tube. After removal of the solvent, the residue was partially distilled at 170 °C and 50 mm pressure onto a clean finger condenser as a drop of clear yellow oil.

(b) *Infra-red Spectrum Analysis*.—The infra-red spectrum was obtained on a Perkin Elmer model 12C spectrometer equipped with 13 cycles amplifier and NaCl optics. Calibration was effected in the usual manner against the data for water vapour and ammonia tabulated by Oetjen, Kao, and Randall (1942).

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## SHORT COMMUNICATIONS

### THE STERIC CONFIGURATION OF EUDESMOL\*

By A. J. BIRCH† and K. M. C. MOSTYN†

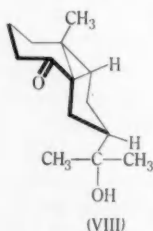
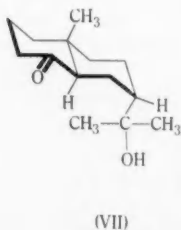
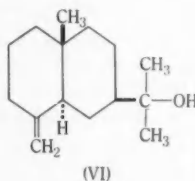
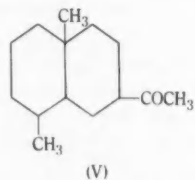
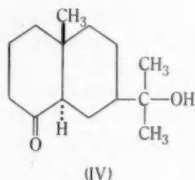
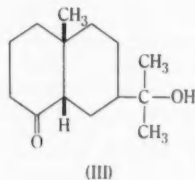
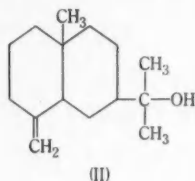
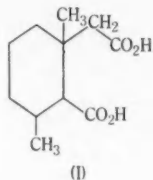
The acid (I), obtained by the degradation of the dihydro-derivative of eudesmol (II) (Ruzicka, Plattner, and Fürst 1941; Plattner, Fürst, and Hellerbach 1947), was found to be capable of isomerization by heating with hydrochloric acid. The conclusion could therefore be drawn that the acidic groups are probably *cis* in the original material. The case is not, however, a simple one and this conclusion is probably incorrect (Barton 1953). Klyne (1953) has shown from optical rotation data that I is almost certainly *trans* fused. In order to provide further evidence we have examined the ozonolysis of eudesmol (II) under the conditions which permitted the isolation from aromadendrene of a sterically unstable ketone (Birch and Lahey 1953). Eudesmol if *cis* fused should give rise to the *cis*-ketone (III), readily isomerized by alkali or acid to the *trans*-ketone (IV) (Hückel 1925). In fact, the same semicarbazone was obtained both before and after treatment of the ketone with sodium hydroxide. The ketone is therefore IV unless inversion has occurred in working-up. The latter eventuality seems unlikely in view of the isolation in a similar manner of the very unstable  $\alpha$ -apoaromadendrone (Birch and Lahey 1953). The *cis*-ketone (III) may be more stable than an ordinary *cis*-1-ketodecahydronaphthalene if the hydroxyisopropyl group is radial (equatorial), VIII the angular methyl being also radial to one ring. Inversion to the *trans* junction VII would place both of these groups in axial (polar) positions. Further examination would therefore be necessary to show that the energy gain by inversion of the ring junction would be sufficient to stabilize this grouping, but from a consideration of models it would appear likely that VIII is unstable with regard to VII.

Assuming at this stage that the simple view, supported by the work of Barton (1953) and Klyne (1953), is correct and that IV represents the ketone, then evidence exists as to the disposition of the hydroxyisopropyl group which permits the assignment of a complete configuration to eudesmol. The ketone (V), obtained by the dehydration and ozonolysis of dihydroeudesmol, regenerates crystalline dihydroeudesmol of unchanged optical rotation by the action of methylmagnesium iodide (Ruzicka, Wind, and Koolhaas 1931). The conditions of working-up this ketone might have been expected to produce at least some epimerization of the acetyl group had it been in an unstable (axial) configuration.

\* Manuscript received February 22, 1954.

† Department of Organic Chemistry, University of Sydney.

It was regenerated by boiling its semicarbazone with aqueous oxalic acid for 4 hr and then distilled at 145–147 °C. The acetyl group must therefore be radial and on the basis of IV the most probable formula for eudesmol is VI.\* Further work is in progress aimed at a decisive conclusion of the problem.



\* Added April 12, 1954.—Since this paper was submitted for publication there has come to our notice a communication to the Editor, *J. Amer. Chem. Soc.* **76**: 313 (1954), by B. Riniker, J. Kalvada, D. Arigoni, A. Fürst, O. Jeger, A. M. Gold, and R. B. Woodward, which puts forward the same steric formula for eudesmol as given above and proves that this is the absolute configuration. Our formula VI is not intended as an indication of the absolute configuration but is merely given arbitrarily as one of the two possible enantiomers.—A.J.B.



### Experimental

(a) *Ozonolysis*.—Eudesmol (10 g) in pure ethyl acetate (200 c.c.) was cooled to 0 °C and a stream of ozonized oxygen (5–7%) bubbled rapidly for 4 hr. The ozonide was decomposed by the action of zinc dust, acetic acid, and water in the cold (Birch and Lahey 1953) or better by catalytic hydrogenation in the presence of palladium charcoal. The same ketone was obtained in both cases. A portion of the solution distilled into 2,4-dinitrophenylhydrazine in 2N hydrochloric acid and worked-up rapidly in order to avoid the formation of acetyl 2,4-dinitrophenylhydrazine gave the expected derivative of formaldehyde as bright yellow needles, m.p. 162 °C undepressed by an authentic specimen, m.p. 164 °C. The ethyl acetate was removed from the rest of the solution by evaporation under reduced pressure leaving a viscous oil. Despite the statement of Ruzicka, Wind, and Koolhaas (1931) the oil could not be induced to crystallize. The oil (1 g) was kept overnight with a solution of semicarbazide hydrochloride (1.5 g) and hydrated sodium acetate (2 g) in ethanol (10 c.c.) and water (20 c.c.). The crystals were removed by filtration and recrystallized from aqueous methanol as colourless plates, m.p. 138 °C,  $[\alpha]_D + 8^\circ$  (in ethanol) (Found: C, 60.9; H, 9.5%. Calc. for  $C_{14}H_{24}O_4N_2 \cdot H_2O$ : C, 60.2; H, 9.7%). The ketone (1 g) was heated on the steam-bath for 30 min in ethanol (10 c.c.) and aqueous sodium hydroxide (10%; 20 c.c.) and the recovered oil treated as above. The same semicarbazone was obtained  $[\alpha]_D + 8^\circ$  (in ethanol), m.p. 138 °C (undepressed by the derivative above).

The authors are indebted to Professor A. K. Macbeth and Mr. A. R. Penfold for gifts of eudesmol.

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## THE REACTION OF CYANOGEN WITH METHYLMAGNESIUM IODIDE AND METHYLMAGNESIUM BROMIDE\*

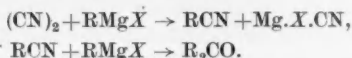
By K. R. LYNN†

Blaise (1901) found that 2 moles of ethylmagnesium bromide reacts with 1 mole of cyanogen to form diethyl ketone rather than the expected dipropionyl. This work was later confirmed and expanded by Grignard and co-workers (Grignard 1911; Grignard and Bellet 1912), who first reported the isolation of nitriles from the interaction of organomagnesium compounds and cyanogen (in the ratio of 1 mole of each reagent), and later, Grignard, Bellet, and Courtot

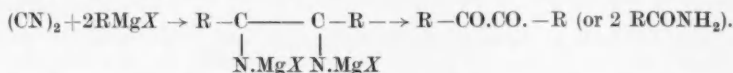
\* Manuscript received February 3, 1954.

† Tracer Elements Investigations, C.S.I.R.O., Melbourne.

(1919) found that either nitriles or ketones may readily be produced. Presumably the reaction proceeds as follows:



In order to prepare  $^{14}\text{C}$  (carbonyl) labelled diacetyl, the interaction of labelled cyanogen with methylmagnesium halides was considered, since cyanogen may readily be prepared in good yield from  $\text{K}^{14}\text{CN}$  (Lynn, unpublished data). An investigation of the reaction at low temperatures was undertaken, as previous workers used temperatures above  $0^\circ\text{C}$ . Among the products isolated were diacetyl and acetamide. These results indicate that the reaction probably proceeds as follows:



Because of the lack of readily available refrigerants in the range  $-80$  to  $-110^\circ\text{C}$ , and since alternative procedures offered higher yields of diacetyl, experiments were not continued.

### Experimental

The experiments were performed with non-radioactive material in a standard vacuum manifold (Calvin *et al.* 1949) working at pressures of the order  $10^{-3}$  to  $10^{-4}$  mm mercury. The cyanogen was generated by heating silver cyanide (Cook and Robinson 1935) on the manifold, the gas obtained being distilled through phosphorus pentoxide twice, then stored until used. The organometallic compounds were prepared as usual, the flasks attached to the vacuum system frozen in liquid oxygen, and evacuated. Methyl bromide and methyl iodide were both investigated in strictly comparable reactions with identical results.

Cyanogen was transferred into the vessel containing 2 moles of the Grignard reagent by means of liquid oxygen (experiments were performed on a 10 m mole scale). This flask was then closed from the rest of the system and allowed to attain dry-ice temperature, after which it was immersed in a bath at  $-70^\circ\text{C}$  and stirred vigorously with a magnetic stirrer as soon as melting of the reaction mixture occurred. Pressure measurements indicated the completion of the reaction within 30 min of melting, though a further 15 min were allowed before decomposition with ice/hydrochloric acid. Extraction with ether simplified the isolation of the products which were found to be diacetyl (c. 10% yield; oxime, m.p.  $245^\circ\text{C}$ ), acetamide (c. 0.1 g, 8%, m.p.  $82^\circ\text{C}$ , hydrolysis producing acetic acid, *p*-nitrobenzyl ester, m.p.  $78^\circ\text{C}$ ), and an unidentified residue.

To confirm the presence of diacetyl further, the ethereal extract of a decomposed reaction mixture was dried and treated with an excess of methylmagnesium bromide (Pace 1928), when pinacol was isolated as one product (m.p.  $40-41^\circ\text{C}$ ; acetate, m.p.  $64^\circ\text{C}$ ) (for each the melting points given above were undepressed on admixture with pure samples).

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